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CONTENTS

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RP	TITLE AND AUTHOR	Page
1700.	Spectrophotometric and colorimetric determination of the colors of the TCCA standard color cards. Genevieve Reimann, Deane B. Judd, and Harry J. Keegan.....[Price 15 cents]	209
1701.	Wearing quality of experimental currency-type paper. Frederick T. Carson and Merle B. Shaw.....[Price 10 cents]	249
1702.	Heats of formation, hydrogenation, and combustion of the monoolefin hydrocarbons through the hexenes, and of the higher 1-alkenes, in the gaseous state at 25° C. Edward J. Prosen and Frederick D. Rossini.....[Price 05 cents]	269
1703.	Studies of binary and ternary combinations of magnesia, calcia, baria, beryllia, alumina, thoria, and zirconia in relation to their use as porcelains. R. F. Geller, P. J. Yavorsky, B. L. Steierman, and A. S. Creamer.....[Price 15 cents]	277
1704.	Analysis of a standard sample of the carburetted water-gas type by laboratories cooperating with the American Society for Testing Materials. Martin Shepherd.....[Price 15 cents]	313

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1700

Part of Journal of Research of the National Bureau of Standards, Volume 36, March 1946

SPECTROPHOTOMETRIC AND COLORIMETRIC DETERMINATION OF THE COLORS OF THE TCCA STANDARD COLOR CARDS

By Genevieve Reimann,[1] Deane B. Judd, and Harry J. Keegan

ABSTRACT

The color cards of the Textile Color Card Association of the United States are widely used in the textile and allied industries and by many procuring agencies of the Federal Government. The Textile Color Card Association issues both seasonal and standard color cards. The seasonal cards provide a color-forecasting service to textile manufacturers and promote color coordination among the trades; the standard cards present colors for which there is a popular and continuing demand. Most important of the color cards is the Standard Color Card of America, the current ninth edition containing 216 colors. Preeminent among the many special sets of color cards issued by the Association for use of the Federal Government is the United States Army Color Card showing 22 official colors for the arms and services. The specification of the colors of the Ninth Edition Standard Color Card and the United States Army Color Card has been undertaken for the purpose of correlating these textile standards with American War Standard Z44–1942 for the specification and description of color. The 238 samples comprising these color cards have been examined by basic spectrophotometric and colorimetric procedures. From this study there have been found daylight reflectance, Y, chromaticity coordinates (x,y), Munsell renotations, and ISCC–NBS color designations for these samples, as recommended by American War Standard Z44–1942. As more than half of these textile standards are fluorescent, and as existing spectrophotometers are not suited to the evaluation of such samples, considerable reliance has been placed on quantitative colorimetric and photometric comparisons with the Munsell color standards, both by means of a chromaticity-difference colorimeter and by the Martens photometer.

As a closing check, Munsell book notations of these textile standards have been obtained by a direct visual comparison with the color scales of the Munsell Book of Color.

CONTENTS

	Page
I. Introduction	210
II. General considerations	211
1. Fluorescence	212
2. Luster	213
III. Method	213
1. Recording spectrophotometer	214
2. Multipurpose reflectometer	216
3. Chromaticity-difference colorimeter	217
4. Macbeth-Martens reflectometer	218
5. Munsell book notations	219
IV. Results	220

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Page

V. Discussion 227
1. Angular conditions 229
2. Metamerism 230
3. Fluorescence 232
4. Munsell book notations 233
VI. Fundamental specification of the Textile Color Card Association standards 235
VII. Summary 246
VIII. References 246

I. INTRODUCTION

Since its formation, growing out of interference with normal communication with Europe in the First World War, the Textile Color Card Association of the United States has performed two distinct services for the textile and allied industries. The first is a color-forecasting service so that the textile manufacturer, dyer, and dyestuff producer may each plan his production with confidence that his choice of colors will be both procurable and salable and will dovetail satisfactorily with that for merchandise from other industries serving the fashion trades. In this way the manufacturer and retailer are protected to a considerable extent from accumulating large stocks of goods that will not sell, and the customer is supplied with a coordinated instead of haphazard selection. The second service is to standardize colors for the textile and allied industries so that the standard name will always signify the same color. By this standardization, the ordering of merchandise is greatly facilitated.

The color standardization is accomplished chiefly by the issuance of the TCCA Standard Color Card of America, which is supplemented by seasonal cards giving the color forecast. All seasonal colors are automatically standardized under the TCCA system of numbering and naming colors. The ninth edition of the Standard Color Card of America [32] [2] was issued in 1941, and includes 216 colors for which there is a continuing demand. These cards are widely used in the textile and allied industries and are there the accepted authority. They are also used in color specification by governmental agencies and by industries quite unrelated to the fashion trades.

In addition to these services to industry, the Textile Color Card Association has cooperated with the procuring agencies of the Federal Government by issuing many special sets of color standards for textiles. Preeminent among these is the United States Army Color Card [33] showing the official colors for the arms and services. This card was originally issued in 1930; it was revised first in 1938 and again in 1943 so as to include 22 colors. It has been approved and accepted by the Quartermaster General, United States Army.

Paralleling the TCCA work, another step to aid the procurement of war goods covered by a color requirement was taken by the American Standards Association. In 1942 there was formulated and issued American War Standard Z44–1942 [1] for the specification and description of color. This standard was intended primarily to assist subcontractors to comply with color requirements by providing a unified set of coordinated procedures for color specification. The standard provides (1) that the spectrophotometer shall be recognized as the basic instrument in color specification, (2) that spectrophotometric

[2] Figures in brackets indicate the literature references at the end of this paper.

data shall be reduced in accord with the methods recommended in 1931 by the International Commission on Illumination [9, 15, 28, 30], (3) that suitably calibrated working standards of color, such as those of the Munsell Book of Color [25] be used wherever applicable, and (4) that if a color designation is required for general comprehensibility, with precision unimportant, the ISCC–NBS method of designating colors be used [18].

The specification of the colors of the ninth edition of the Standard Color Card of America and of those of the United States Army Color Card has been undertaken for the purpose of correlating these textile standards with the general methods covered by Z44–1942. Some of the fruits of this correlation have already been garnered in the form of information supplied in advance of publication to war agencies that have to write specifications of color requirements for goods that they desire to procure. It is the purpose of the present paper to describe the measurements made of the textile samples, to give the adopted colorimetric results in the form recommended by Z44–1942, and to describe the checks by means of which the accuracy of the adopted values has been established.

II. GENERAL CONSIDERATIONS

The samples of the ninth edition of the Standard Color Card of America are made of satin-finish pure-dye silk, the back, or matte side, being displayed over most of the area of each. The samples of the Army card are of pure-dye silk ribbon, half of satin-finish, half of grosgrain, or ribbed, finish. The brilliance of many of the colors of both sets is partly due to the use of fluorescent dyes. The high luster of the silk fibers and the fluorescence of the dyes combine to interpose formidable obstacles to the colorimetry of these samples, and have a determining influence upon the choice of method.

It is obvious that to be generally useful the correlation between the TCCA standards and nonfluorescent nonlustrous working standards, such as the Munsell standards, evaluated according to Z44–1942, must hold for comparison of such samples in natural diffused daylight near a window. This is the customary condition under which such comparisons are carried out. This requirement gives an approximate definition both of the spectral distribution of the illumination which has to be adopted and of its angular distribution. As sufficiently close to the spectral character of average natural diffused daylight, ICI standard illuminant *C* [9, 15, 28] as recommended by Z44–1942, or alternatively, Macbeth artificial daylight [28] at a color temperature of about 6,800° K has been taken in this work. To characterize the desired angular distribution, illumination incident on the samples along angles spreading through a range of 50° to 70°, roughly centering upon an angle of 45° from the surface has been taken. Standard angular conditions are not specified in Z44–1942 nor are there spectrophotometers or colorimeters available that conform even within these rather wide tolerances. Only near a north window in the daytime or by installations of artificial daylight particularly designed for the purpose are these requirements fulfilled. The general principle of the method, therefore, is to make visual estimations of the Munsell book notations of the 238 samples under these conditions, then to measure the samples with available instru-

ments, and compare the results. It has been found possible to reduce the data in a systematic way yielding no important discrepancy between instrumental result and visual estimate. Incidental to the development of methods of reducing the data in accord with this principle, the discrepancies that would arise through routine application of methods customary for nonlustrous, nonfluorescent samples have been evaluated.

1. FLUORESCENCE

The difficulties involved in the measurement of lustrous and fluorescent textile samples are well known, but some of them will now be recalled. A fluorescent sample is one that when irradiated by energy of one wavelength emits energy of a different (usually greater) wavelength. The complete specification of such a sample requires a separate analysis of the emitted energy for irradiation of the sample by each portion of the spectrum eliciting fluorescence in addition to the usual spectrophotometric analysis covering the entire visible spectrum; that is, instead of one spectrophotometric curve, there would have to be obtained a whole set of them; instead of one column of tabulated values, there would be required several, perhaps as many as 30 columns; instead of being restricted to the visible spectrum, evaluation of fluorescence at least for irradiation by the near ultraviolet portion of the spectrum of the standard illuminant would have to be included. No existing recording photoelectric spectrophotometer is provided with means to disperse both the incident and emitted energy, and, therefore, accurate spectrophotometric analysis of fluorescent samples is not now feasible.

Despite the fact that many commercial materials are fluorescent to a detectable degree, such materials have often been studied by the spectrophotometer in the usual routine way with useful results. Although important exceptions have been noted [5], it has been customary to assume that the degree of the fluorescence of such samples is too slight to invalidate the measurements, just as it has been assumed that samples whose fluorescence is not detectable by visual examination may safely be so measured. All the 238 samples were accordingly examined for fluorescence, both for excitation by ultraviolet energy from a mercury arc and filter and by energy from an incandescent lamp and a green gelatin filter. Doubtful samples were also examined for excitation by each portion of the visible spectrum by energy from the monochromator of a spectrophotometer. More than half were found to be noticeably fluorescent, and an attempt was made to judge whether the fluorescence was strong or weak, but it was, of course, impossible to judge whether the fluorescence of a given sample would or would not introduce a significant error in the measurements. Checks, both instrumental and visual, were therefore carried out, as will be presently described, and if these checks failed to agree well with the spectrophotometric result, the sample was usually classified as strongly fluorescent, although other sources of discrepancy also had to be given consideration.

Samples that fluoresce strongly for excitation by ultraviolet energy require more rigid control of the spectral composition of the illuminant than nonfluorescent samples. The question may be raised, for example, whether Macbeth artificial daylight at a color temperature

of 6,800° K, known to be a close representative of average natural diffused daylight transmitted by window glass insofar as intercomparison of nonfluorescent samples is concerned, is sufficiently close to it for strongly fluorescent samples. Visual checks by natural daylight have therefore been made for all strongly fluorescent samples evaluated by colorimetric comparisons under Macbeth daylight.

2. LUSTER

Difficulties arising from the luster of the fibers composing the samples are of two sorts. Because of the regularity of the fabric weave, light striking the samples from some one direction, say perpendicularly, is incident obliquely on many regularly recurring elements of the fiber surface and is reflected, either directly or after incidence on one or more fiber surfaces, and leaves the sample in a partially polarized state. If polarizing instruments are used for the measurement, special precautions have to be taken [3, 23]. Another difficulty arises from the dependence of the appearance or color of the sample on the directions according to which it is illuminated and viewed. There are two rather widely used conditions of illuminating and viewing samples for colorimetry. One is to illuminate the sample at 45° and view it perpendicularly [30], or the reciprocal condition of perpendicular illumination and 45° viewing, which is equivalent [22]. The other is to illuminate the sample diffusely and view it perpendicularly [23], or the equivalent reciprocal condition [11, 12]. It will be noted that neither of these observing conditions conforms exactly to observation near a window, although each agrees in one respect—45°-normal agrees insofar as light from a window comes preponderantly from the direction of about 45°; diffuse-normal agrees insofar as light from a window is diffused to a considerable degree. Information is to be given as to the degree to which the colors of the TCCA standards vary, depending upon which of these conditions is used.

III. METHOD

The present measurements were carried out on 4-inch-square samples of the Standard Color Card of America supplied especially for these studies by the Textile Color Card Association. The measurements were made on the matte side of the samples; none were made on the shiny side. Five of the Army cards were also supplied, and measurements were made on the grosgrain portions only. Figure 1, A, is a photomicrograph (magnification 18 diameters) of the matte portion of a sample (Terra Cotta, 70161) of the standard card; figure 1, B, shows similarly the grosgrain portion of a sample (Brick Red, 65020) from the Army card. Although these views show only the matte portions of the samples, the highlights revealing either surface-reflected light or light that has penetrated only one or two fibers are clearly evident.

In addition to the instrumental measurements, all samples in the official copy of the Standard Color Card of America that had been placed in the vaults of the National Bureau of Standards early in 1942, all samples of the Army card, and many of the 4-inch-square samples were compared with the color scales of the Munsell Book of Color. The 4-inch-square samples were also compared with the corresponding sample in the official copy.

1. RECORDING SPECTROPHOTOMETER

Four-inch-square samples of the fabrics of the standard color card were prepared for spectrophotometric measurement by doubling and backing them with white cardboard similar to that used in the card itself. The white cardboard was attached to a wooden block cut to angles needed for consistent alinement of the sample. For the colors of the Army card, composite samples were made up by mounting four rows of ribbon overlapping on a white cardboard in such a way that only the grosgrain portion was presented for measurement. The spectrophotometer was the General Electric photoelectric recording type [10, 24], an instrument with slits transmitting a 4-mμ spectral band being used for the samples of the Army card and for about one-third of the samples of the standard card, the remainder being measured by means of an instrument with 10-mμ slits. The instrument using a 4-mμ band irradiates the samples along the perpendicular; that using a 10-mμ band at 6°. Both instruments collect the energy reflected in all directions, except for a small solid angle centering on the direction of mirror reflection. Tests indicated that slight discrepancies possibly ascribable to the different characteristics of the two instruments were considerably less than differences that were obtained by measuring a different area of the sample on the same instrument.

Each curve sheet was completely calibrated [6] and the samples were run twice, first with the ridges at 45° from the vertical, second with the sample rotated in its own plane through 90° from the first position. Figure 2 shows a typical curve sheet with zero line, the Vitrolite curve that was used in lieu of the 100-percent curve, and the didymium-glass curve that was used for calibration of the wavelength scale. These instruments measure spectral reflectance for nearly perpendicular incidence relative to that of magnesium oxide [29], which is numerically equal to directional reflectance for diffuse illumination and nearly perpendicular viewing. The wavelength-scale corrections were determined and applied, the curves were read twice independently through the aid of a mechanical and optical device developed by one of us [31] (GBR) to present to the operator a magnified image of the reflectance scale, the corrected wavelength scale, and the spectrophotometric curve close to the point to be read. Readings differing by 0.002 or more were repeated a second time. In this way the spectral reflectance of each sample relative to that of magnesium oxide was determined and checked for each 10-mμ interval from 400 to 750 mμ. Values of spectral reflectance were extrapolated to 380 and 770 mμ and luminous reflectance relative to magnesium oxide, Y, and chromaticity coordinates, x and y, were computed by the method of 10-mμ summation [28].

Possible sources of error in the measurements of the samples of the Army card are small variations in color from one ribbon to another from which the composite sample was made. Furthermore, the area viewed by the spectrophotometer was not completely filled by the grosgrain portion of the sample, a small fraction of the area being unavoidably occupied by the salvage and possibly a small portion of the satin-finish of one of the five ribbons. Care was taken, however, to insert the sample so that the beam fell entirely on the grosgrain

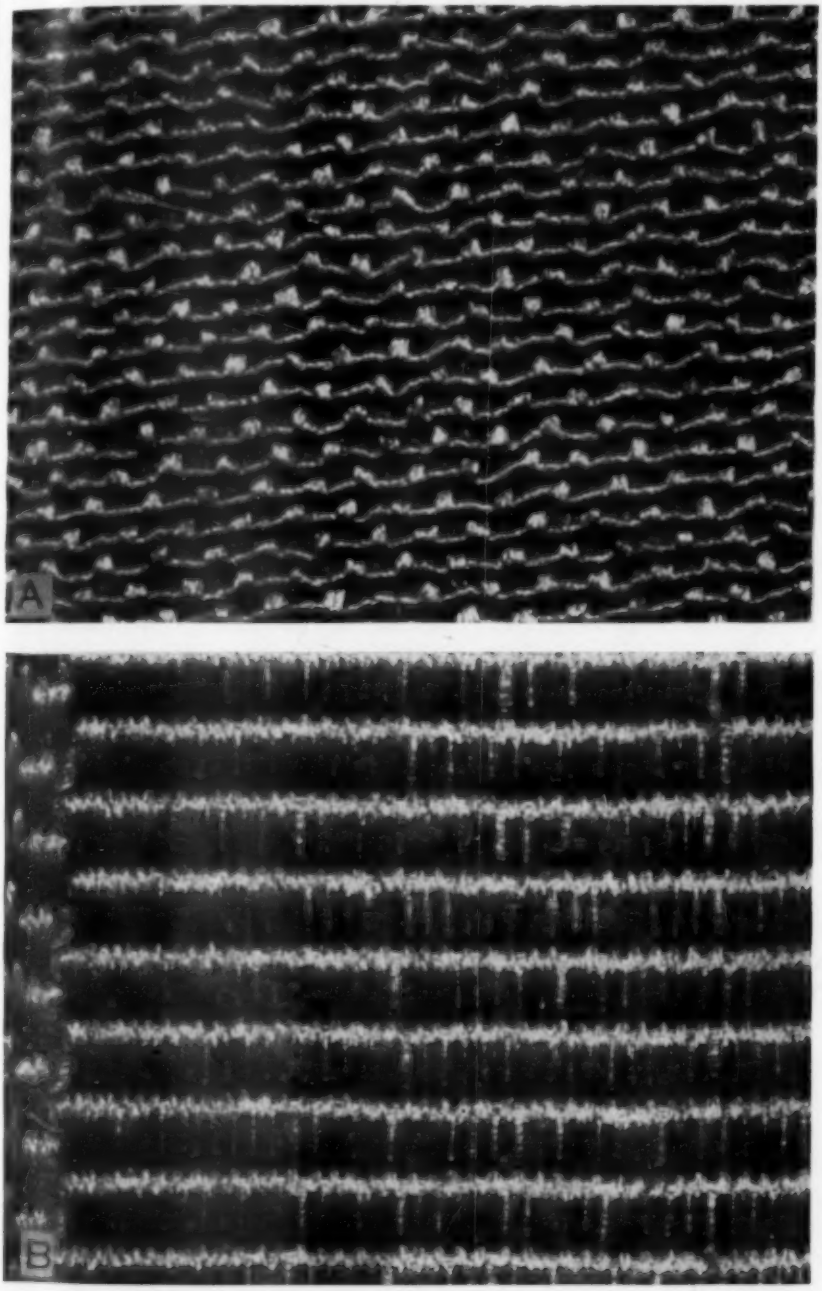
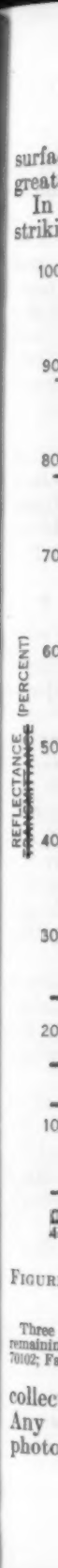


FIGURE 1.—*Photomicrographs showing the weave of the fabric samples measured.*

A, Terra Cotta (70161) from the Standard Color Card of America. B, Brick Red (65020) from the United States Army Color Card. The illumination was at 45°; the direction of view, perpendicular to the gross plane of the sample. Note the presence of many highlights, indicating surface-reflected light.


REFLECTANCE (PERCENT)
TRANSMITTANCE

surface. Subsequent checks failed to reveal uncertainties significantly greater for these samples than for the samples of the standard card.

In this type of spectrophotometer the energy is dispersed before striking the sample, but not after striking it. The reflected energy is

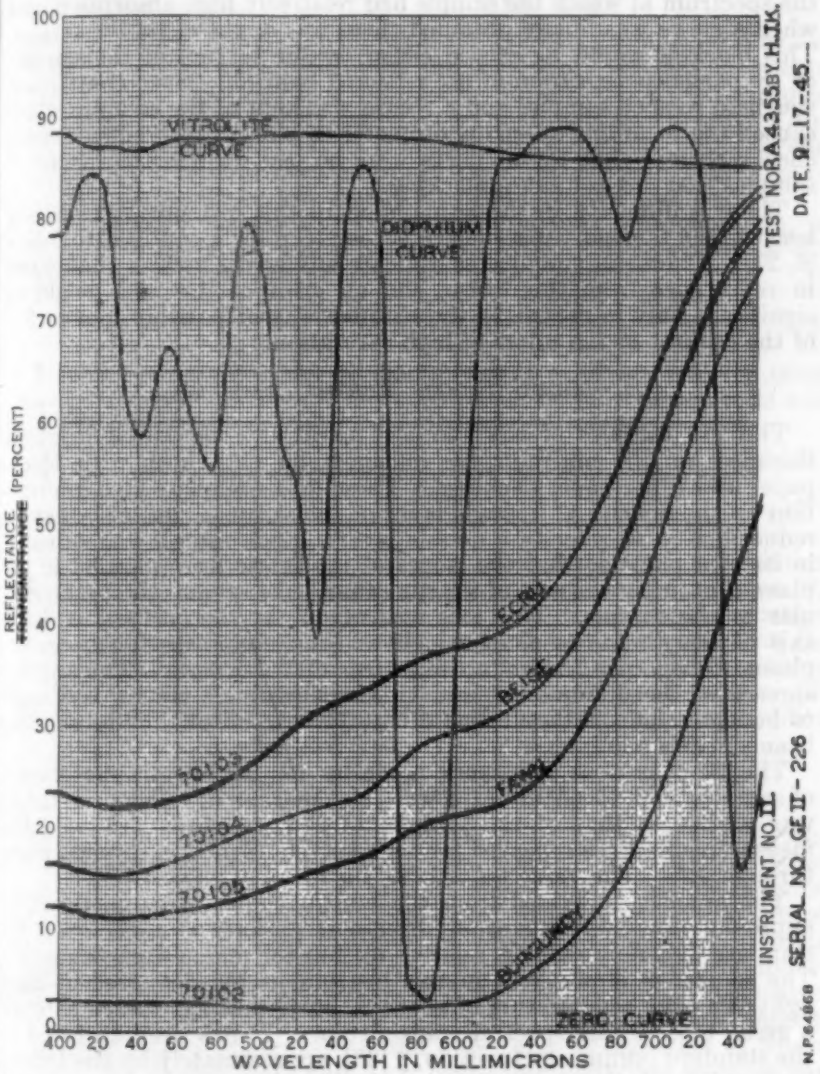


FIGURE 2.—*Typical curve sheet drawn by recording spectrophotometer with 10-mμ spectral band.*

Three of the seven curves shown are for calibration (zero curve, vitrolite curve, didymium curve); the remaining four indicate spectral reflectance of samples from the Standard Color Card of America (Burgundy, 70102; Fawn, 70105; Beige, 70104; and Ecru, 70103).

collected by an integrating sphere and is responded to by a photocell. Any energy emitted by fluorescence is also likely to actuate the photocell because of its relatively high response to long-wave energy,

and as it is counted by the instrument as having the wavelength of the incident energy, an error of greater or less importance must result [5].

Some of the samples caused the instrument to block at a portion of the spectrum at which the sample had relatively high absorption, and when a curve was finally obtained there was doubt of its correctness. This blocking might be caused either by the texture of the samples or by partial polarization of the reflected light [3]. Special attention was paid to such samples and a record was kept of the samples which caused the recording spectrophotometer to block. Subsequent cross-checks showed that these curves were no less reliable than those of samples that did not cause blocking.

There is difficulty in the adjustment of this instrument near zero because the tangent-square curve is too steep for a cam rod to follow [6, 24]. Checks have failed to indicate any errors greater than 0.003 in reflectance from this cause, and an error of this size would be significant only in regard to the chromaticity of possibly four or five of the darkest of the colors of high saturation.

2. MULTIPURPOSE REFLECTOMETER

The 216 samples of the standard card were measured in single thickness on the multipurpose reflectometer [13], both with black-paper and white-paper backings. These measurements give information on the opacity of a single layer of the samples, and also may be reduced so as to refer to a double layer. Each sample was oriented in its own plane so that the ridges of the fabric were parallel to the plane containing the axis of the illuminating beam and the perpendicular to the sample. This axis was at 45° to the surface, and the axis of the directions along which reflected light can fall upon the photocell is perpendicular to the surface of the sample. The angular spreads of the illuminating and viewing directions are far too small to be equivalent to the desired 50° to 70° spread of the illuminating beams near a window.

The 22 composite specimens made up for the spectrophotometry of samples from the Army card were also measured. The orientation was similar to that of the samples of the standard card, and the measurements were repeated for each sample turned in its own plane through 90°. The value reported is the mean of these two.

The quantity obtained from the multipurpose reflectometer is an approximation to 45°-normal directional luminous reflectance for standard ICI illuminant C relative to that for magnesium oxide [29]. The sample is illuminated in this instrument by incandescent-lamp light at a color temperature of about 3,100°K that has passed through a green filter whose spectral transmittance, T, has been adjusted to the standard luminosity function, $\bar{y}$ [28], approximately by the following condition [14]:

$$T=kE_c\bar{y}/E_sS, \tag{1}$$

where E_c is the spectral irradiance of ICI standard illuminant C [9, 15, 28], E_s is the spectral irradiance from a complete radiator at a temperature of 3,100°K, and S is the spectral sensitivity of the photocell. If the filter satisfied eq 1 perfectly, the instrument should be perfectly applicable to the measurement of matte nonfluorescent

samples. Computations based upon the actual values of T were made to establish the limits of error ascribable to failure of T to comply with eq 1, and it was found that the maximum such error possible with these textile samples corresponds to about 0.3 Munsell value step.

As the actual illuminant differs from average daylight, and as the evaluation of the reflected flux by the bare photocell does not accord with that by the standard luminosity function, the multipurpose reflectometer, like the recording spectrophotometer, evaluates the fluorescent energy in a way that is generally different from its evaluation by a normal observer and must therefore be expected to produce an error of greater or less extent for all fluorescent samples.

In order to evaluate the directional luminous reflectance, R_2, of two layers backed by white paper, the data for the samples of the standard card were reduced according to the formula

$$R_2 = aR_w + bR_b, \tag{2}$$

where R_w and R_b are the measured values of directional luminous reflectance over white and black backings of reflectances 0.82 and 0.04, respectively, and a and b are weighting factors defined as

$$\left.\begin{aligned} a &\equiv (1/0.78)\ [(R_w+R_b)/2-0.04], \\ b &\equiv (1/0.78)\ [0.82-(R_w+R_b)/2]. \end{aligned}\right\} \tag{2a}$$

Formula 2 agrees closely with the Kubelka-Munk formulation [16, 20] for nonselective specimens, and the difference between R_w and R_b was found to be sufficiently small that no closer approximation seemed to be warranted. If it was found that R_w was less than R_b, the weights a and b were both set equal to 1/2. This condition was satisfied by a good many measurements of dark samples for which R_w and R_b must be expected to differ but little and was ascribed to unavoidable experimental error.

3. CHROMATICITY-DIFFERENCE COLORIMETER

Each of the 238 samples was compared by means of the chromaticity-difference colorimeter [17] with another TCCA sample of nearly the same color or with at least one of the Munsell standards. This comparison served as a cross-check on chromaticity errors of whatever cause, and also checked the classification of the sample as to importance of the fluorescence. This instrument has been modified since its original description [17] by installation of stray-light traps in the position of mirror reflection from the test and comparison samples into the Lummer-Brodhun cube, and by insertion of filters of Corning Daylite glass and Aklo heat-absorbing glass between the light source and the samples instead of the Daylite glass in the eyepiece. The samples are thus illuminated by artificial daylight of closely the same spectral composition as that produced by the Macbeth lamp of color temperature 6,800°K. The light is incident nearly along the perpendicular and the samples are viewed at 45° to the surface. Each sample was used in double thickness backed by white cardboard, and was oriented in its own plane so that the ridges of the fabric were parallel to the plane containing the viewing direction and

the perpendicular to the sample. The angular spreads of the illuminating and viewing directions are far too small to be equivalent to the desired 50° to 70° spread of the illuminating beams near a window. Each Munsell standard was backed by a white card or a black card to correspond to the backing used in its original spectrophotometric calibration [7, 19].

By calibration of the wedges of yellowish and greenish glass, by means of which a chromaticity match is procured in the 9 by 13° double-trapezoid field of this instrument, the chromaticity difference between the two samples compared can be expressed in terms of the chromaticity coordinates, x and y, of the standard ICI system. Comparison of these differences with those obtained by means of the spectrophotometer serves to disclose most of the important errors in chromaticity coordinates. If the comparison is made with a previously measured Munsell standard [7, 19], the differences in chromaticity coordinates, x and y, may be added to the known values for the standard, and chromaticity coordinates, x and y, found for the sample. This was done for each sample classified as strongly fluorescent. It is to be noted that the illuminant used in this instrument conforms to the requirement that the spectral composition be essentially that of average natural daylight. Furthermore, the reflected light is evaluated by comparison with that from a nonfluorescent sample by means of an observer (either GBR, or both GBR and DBJ) at least approximately equivalent to the standard ICI observer. The method is therefore applicable to strongly fluorescent as well as nonfluorescent samples.

4. MACBETH-MARTENS REFLECTOMETER

Each of the 50 or more samples classified as strongly fluorescent were compared in double thickness to a Munsell standard of nearly the same color by means of a Macbeth lamp [28] and a Martens photometer [21]. The illumination centered about 45° to the sample surface and was somewhat diffused, as it came partly from the frosted bulb and partly from a white reflector by transmission through a 7-inch glass roundel ground on one side and separated from the sample by only 8 inches. The angular spread of the illumination was therefore about 48°, which seems to conform nearly to the desired angular spread of 50° to 70° taken to be representative of viewing by a window. Actually, however, visual comparisons as well as photometric measurements made under this illuminant were found to differ importantly from those made before a window illuminated by light from the sky. These comparisons agreed closely with measurements by the multipurpose reflectometer having much smaller angular spreads. This agreement was taken to indicate that the distribution of the illumination within this 48° spread, which is far from uniform, corresponds much more closely to unidirectional illumination at about 45° than to illumination diffused uniformly throughout a 48° spread. The direction of observation was about 7° from the perpendicular, the deviation from zero being introduced by the biprism of the Martens photometer, whose axis was at 0°.

Each sample was oriented in its own plane so that the ridges of the fabric were parallel to the plane containing the axis of the illuminating beam and the axis of the Martens photometer. The photometer was adjusted for equality of brightness between the two half fields and

angle θ_1 was noted. Then the sample and standard were interchanged, the photometer reset for a brightness match, and angle θ_2 noted. The directional luminous reflectance, R_2, of the sample in double thickness was computed from the formula

$$R_2 \equiv R_s \tan(\theta_1) \cot(\theta_2), \tag{3}$$

where R_s is the published luminous reflectance [7, 19] for the Munsell standard evaluated from spectrophotometric measurement for perpendicular illumination. There is a correction to be applied to R_2 found by this formula if the light reflected from the sample is not in the same state of polarization as that from the standard [23]. Measurement of the polarization of these beams for a few pairs that were compared indicated that the correction in no case would exceed 0.001, and accordingly no corrections were applied.

It will be noted that in this comparison the fluorescent sample is illuminated by a suitably close representative of natural daylight; and as with the chromaticity-difference colorimeter the reflected light is evaluated by comparison with that from a nonfluorescent standard by means of an observer at least approximately equivalent to the standard ICI observer. The method is therefore applicable to strongly fluorescent as well as to nonfluorescent samples.

5. MUNSELL BOOK NOTATIONS

Each of the 238 mounted samples was compared with the color scales of the Munsell Book of Color (complete 40-hue-chart edition, 1929 and 1942 [25]) by one observer (GBR) and Munsell book notation found in the usual way by visual interpolation and extrapolation along these scales. Some of these notations were checked by similar comparisons by one (GBR) or two (GBR, DBJ) observers with the unmounted samples used in the measurements. The samples and scales were placed in closely the same plane and illuminated at approximately 45° by light from the north sky passing through a window of such size as to yield an angular spread of directions of illumination between 50° and 70°. The samples were oriented so that the ridges of the fabric were parallel to the plane containing the central direction of illumination and the perpendicular to the sample. The direction of view was nearly perpendicular to the surfaces of the samples.

The Munsell book notation so found for each sample was converted into chromaticity coordinates, x and y, by interpolation and extrapolation on large-scale (x,y)-charts prepared for that purpose by Marion A. Belknap. These charts are similar to figures 2 to 8 of Research Paper RP1549 [19] and include points corresponding to the measurements of the third intermediate hues [7], and they include also broken lines for each chroma and each hue step to facilitate linear interpolation between the plotted points.

From the Munsell book notations there were also found estimates of daylight reflectance, Y. These estimates were found by converting book-notation value first into renotation value by adding to the book-notation value of the textile sample the average difference between the renotation and book-notation values of the neighboring Munsell samples. In taking this average the various differences were given weights either of zero or of one, in accord with the principle of counting

one or both of two neighboring standards, depending on whether the unknown is very close to one or about equally distant from both. This accords with the technic of making the visual interpolations—if the hue of the unknown is very close to that of one of the constant-hue charts of the Munsell book, no attention is paid to other hue charts, but if the hue of the unknown is about midway between that of two charts, both are used. Similar considerations apply to Munsell value and chroma. Thus, the largest number of Munsell samples that could be given a weight different from zero in taking the average is eight; the smallest number is one. The division of the Munsell hue, value, and chroma scales according to whether the weight is to be zero or one is indicated by table 1, which gives an example of the division near 5R 4/2. The rule followed is to weight the samples equally throughout the central third of the interval between them, and outside of this central interval, to weight only the nearest sample.

TABLE 1.—*Division of the hue, value, and chroma scales according to whether one or both of the samples defining an interval is to be used in deriving renotation value from book-notation value (example near 5R 4/2)*

Hue scale	Weight of—		Value scale	Weight of—		Chroma scale	Weight of—	
	5.0R	7.5R		4.0	5.0		2.0	4.0
5.0R	1	0	4.00	1	0	2.0	1	0
.1	1	0	4.05	1	0	2.1	1	0
.2	1	0	4.10	1	0	2.2	1	0
.3	1	0	4.15	1	0	2.3	1	0
.4	1	0	4.20	1	0	2.4	1	0
5.5	1	0	4.25	1	0	2.5	1	0
.6	1	0	4.30	1	0	2.6	1	0
.7	1	0	4.35	1	1	2.7	1	1
.8	1	0	4.40	1	1	2.8	1	1
.9	1	1	4.45	1	1	2.9	1	1
6.0	1	1	4.50	1	1	3.0	1	1
.1	1	1	4.55	1	1	3.1	1	1
.2	1	1	4.60	1	1	3.2	1	1
.3	1	1	4.65	1	1	3.3	1	1
.4	1	1	4.70	0	1	3.4	0	1
6.5	1	1	4.75	0	1	3.5	0	1
.6	1	1	4.80	0	1	3.6	0	1
.7	0	1	4.85	0	1	3.7	0	1
.8	0	1	4.90	0	1	3.8	0	1
.9	0	1	4.95	0	1	3.9	0	1
7.0	0	1	5.00	0	1	4.0	0	1
.1	0	1						
.2	0	1						
.3	0	1						
.4	0	1						
7.5R	0	1						

The differences between renotation value and book-notation value were found from table III of the Final Report of the OSA Subcommittee on the Spacing of the Munsell Colors [26]. These differences were weighted as in table 1 and averaged. The average difference was applied to the book-notation value to find the renotation value. Renotation values were converted into daylight reflectance, Y, by means of table II of the same report.

IV. RESULTS

Table 2, A, gives daylight reflectance relative to freshly prepared magnesium oxide, Y, and chromaticity coordinates, x and y, obtained for the samples of the standard card by all the various methods just described. The samples have been divided into three groups, (1) non-

fluorescent, (2) weakly fluorescent, and (3) strongly fluorescent. Samples for which no fluorescence could be detected by visual examination were classed as nonfluorescent. Samples yielding fluorescence that is visually striking were classed as strongly fluorescent. In addition, three samples tentatively classed as weakly fluorescent (70074, 70103, 70207) were included in the strongly fluorescent group because of studies which showed that the spectrophotometric analysis failed to agree with the estimated Munsell book notation by appreciable amounts that could not be ascribed to any other source of discrepancy. The remaining samples were classed as weakly fluorescent. The instrumental results of table 2, A, form the basis on which final values have been adopted; those derived from the estimations of Munsell book notation serve as a guide to the analysis and interpretation of the instrumental data, but have not been given any weight in computing the final averages. Table 2, B, gives similar results for the samples of the Army card.

TABLE 2.—*Summary of measurements of daylight reflectance relative to magnesium oxide, Y, and chromaticity coordinates, x and y*

A. STANDARD COLOR CARD OF AMERICA

TCCA cable number	Daylight reflectance, Y						Chromaticity coordinates, x and y					
	Multipurpose			Spectrophotometer	Macbeth Martens	Visual estimate via Munsell scales	Spectrophotometer		Subtractive colorimeter		Visual estimate via Munsell scales	
	White backing	Black backing	From eq 2				x	y	x	y	x	y
NONFLUORESCENT SAMPLES												
70023	0.089	0.089	0.089	0.110	0.096	0.096	0.199	0.257	.....	.....	0.197	0.252
70024	.045	.042	.042	.052	.....	.057	.201	.264	0.193	0.258	.18	.26
70033	.222	.215	.217	.228	.....	.22	.305	.370	.....	.....	.312	.374
70034	.160	.159	.159	.173	.....	.16	.315	.355	.....	.....	.312	.352
70035	.080	.079	.079	.096	.....	.096	.307	.365	.305	.362	.310	.372
70036	.037	.037	.037	.044	.....	.050	.302	.377	.....	.....	.309	.379
70044	.147	.145	.146	.160	.....	.148	.249	.254	.....	.....	.253	.259
70045	.106	.105	.105	.127	.....	.134	.239	.250	.....	.....	.243	.253
70046	.065	.068	.068	.078	.....	.082	.231	.235	.....	.....	.238	.240
70047	.052	.051	.051	.065	.....	.061	.214	.215	.....	.....	.21	.22
70048	.036	.036	.036	.047	.....	.046	.227	.221	.....	.....	.223	.221
70060	.021	.021	.021	.024	.....	.026	.238	.147	.231	.158	.25	.18
70061	.337	.323	.328	.358	.....	.34	.353	.459	.....	.....	.349	.461
70062	.272	.267	.268	.301	.....	.30	.324	.458	.....	.....	.322	.467
70065	.064	.064	.064	.074	.....	.080	.264	.397	.....	.....	.264	.404
70066	.035	.036	.036	.040	.....	.050	.273	.371	.283	.364	.294	.361
70068	.561	.463	.523	.537	.505	.51	.480	.447	.489	.453	.474	.447
70069	.396	.351	.370	.380	.....	.36	.516	.419	.....	.....	.512	.418
70070	.372	.325	.344	.358	.327	.34	.519	.406	.....	.....	.515	.411
70071	.274	.250	.257	.262	.....	.25	.555	.386	.....	.....	.556	.388
70075	.032	.033	.032	.038	.....	.037	.218	.174	.229	.181	.227	.184
70076	.020	.025	.022	.029	.....	.034	.230	.194	.239	.204	.242	.206
70077	.018	.018	.018	.021	.....	.022	.245	.221	.262	.236	.263	.238
70078	.018	.017	.017	.020	.....	.020	.256	.238	.272	.248	.269	.247
70085	.070	.068	.068	.083	.....	.077	.213	.187	.204	.179	.218	.191
70086	.055	.055	.055	.061	.....	.061	.201	.163	.199	.156	.206	.174
70087	.031	.031	.031	.040	.....	.046	.189	.148	.190	.141	.198	.153
70088	.033	.033	.033	.036	.....	.043	.232	.216	.232	.221	.241	.227
70089	.016	.022	.019	.026	.....	.031	.240	.230	.....	.....	.245	.236
70090	.016	.016	.016	.018	.....	.018	.263	.255	.....	.....	.273	.269
70092	.239	.229	.231	.237	.224	.21	.393	.366	.....	.....	.389	.365
70093	.175	.169	.170	.176	.....	.16	.392	.362	.....	.....	.395	.366
70094	.113	.112	.113	.125	.....	.114	.411	.366	.....	.....	.419	.366
70095	.047	.048	.048	.048	.042	.057	.418	.358	.....	.....	.412	.361
70096	.039	.038	.038	.045	.....	.037	.347	.331	.....	.....	.345	.331

TABLE 2.—*Summary of measurements of daylight reflectance relative to magnesium oxide, Y, and chromaticity coordinates, x and y*—Continued

A. STANDARD COLOR CARD OF AMERICA—Continued

TCCA cable number	Daylight reflectance, Y						Chromaticity coordinates, x and y					
	Multipurpose			Spectrophotometer	Macbeth Martens	Visual estimate via Munsell scales	Spectrophotometer		Subtractive colorimeter		Visual estimate via Munsell scales	
	White backing	Black backing	From eq 2				x	y	x	y	x	y
NONFLUORESCENT SAMPLES—continued												
70102	0.026	0.025	0.025	0.028	.....	0.028	0.354	0.289	.....	.....	0.365	0.290
70105	.169	.165	.166	.180	.....	.18	.370	.356	.....	.....	.375	.361
70106	.116	.115	.115	129	.....	.127	.366	.351	.....	.....	.376	.353
70107	.050	.052	.052	.053	.....	.063	.396	.363	.....	.....	.395	.362
70108	.037	.036	.036	.039	.....	.046	.357	.342	.....	.....	.372	.353
70111	.081	.080	.080	.092	.....	.093	.279	.286	.....	.....	.284	.289
70112	.066	.066	.066	.071	.....	.066	.271	.276	.....	.....	.282	.286
70113	.061	.059	.059	.070	.....	.070	.275	.271	.....	.....	.283	.281
70114	.020	.027	.024	.030	.....	.034	.267	.261	.....	.....	.286	.273
70117	.204	.196	.198	.211	.....	.21	.430	.380	.....	.....	.413	.369
70119	.064	.062	.063	.069	.....	.075	.441	.368	.....	.....	.428	.364
70120	.041	.040	.040	.044	.....	.050	.431	.354	.....	.....	.423	.362
70125	.183	.180	.180	.189	.....	.18	.416	.331	0.429	0.332	.406	.330
70129	.173	.172	.172	.182	.....	.19	.414	.387	.....	.....	.418	.392
70130	.169	.167	.167	.186	.....	.18	.310	.352	.....	.....	.304	.351
70131	.126	.123	.123	.143	.....	.127	.284	.346	.....	.....	.290	.347
70132	.034	.034	.034	.040	.....	.043	.267	.337	.....	.....	.278	.336
70134	.094	.094	.094	.105	.....	.104	.306	.226	.....	.....	.306	.229
70136	.412	.386	.398	.400	.....	.43	.336	.341	.....	.....	.330	.336
70137	.070	.071	.071	.081	.....	.075	.342	.340	.....	.....	.340	.336
70138	.055	.051	.051	.058	.....	.061	.340	.336	.....	.....	.331	.328
70140	.126	.125	.125	.136	.....	.127	.401	.355	.....	.....	.402	.355
70141	.046	.046	.046	.050	.....	.057	.416	.355	.....	.....	.407	.355
70143	.116	.117	.116	.130	.....	.141	.230	.246	.....	.....	.241	.253
70144	.076	.075	.075	.090	.....	.085	.239	.245	.....	.....	.236	.244
70145	.252	.245	.247	.261	.....	.27	.270	.315	.....	.....	.276	.316
70146	.126	.123	.123	.152	.....	.134	.290	.303	.....	.....	.264	.306
70147	.058	.056	.056	.068	.....	.061	.234	.272	.221	.266	.237	.278
70153	.163	.159	.160	.172	.....	.17	.300	.307	.....	.....	.307	.307
70154	.288	.273	.278	.283	.....	.27	.380	.450	.....	.....	.383	.460
70155	.184	.179	.180	.204	.....	.20	.375	.441	.....	.....	.371	.445
70156	.074	.072	.072	.080	.....	.085	.358	.421	.364	.424	.352	.409
70157	.304	.300	.301	.315	.....	.32	.433	.428	.....	.....	.426	.422
70158	.263	.256	.258	.265	.....	.28	.445	.427	.....	.....	.434	.428
70159	.077	.074	.074	.091	.....	.085	.414	.402	.....	.....	.44	.43
70163	.101	.100	.100	.110	.....	.114	.343	.256	.346	.252	.337	.262
70164	.024	.024	.024	.026	.....	.031	.311	.237	.....	.....	.313	.249
70165	.024	.023	.023	.026	.....	.026	.305	.268	.313	.281	.309	.287
70167	.144	.143	.142	.159	.....	.16	.242	.450	.246	.462	.247	.459
70168	.069	.071	.071	.082	.....	.090	.224	.460	.....	.....	.239	.459
70170	.184	.188	.187	.196	.....	.20	.325	.317	.....	.....	.320	.315
70171	.055	.054	.054	.058	.....	.061	.321	.316	.....	.....	.312	.310
70176	.081	.082	.082	.097	.....	.090	.225	.254	.....	.....	.223	.250
70177	.075	.076	.076	.091	.....	.087	.220	.235	.....	.....	.222	.242
70186	.081	.080	.080	.094	0.080	.096	.318	.319	.....	.....	.321	.328
70188	.263	.263	.263	.279	.....	.28	.366	.365	.....	.....	.367	.368
70190	.038	.037	.037	.042	.....	.044	.362	.260	.368	.265	.366	.272
70192	.092	.092	.092	.102	.....	.096	.419	.353	.425	.353	.419	.348
70198	.200	.194	.195	.208	.....	.20	.378	.367	.....	.....	.382	.371
WEAKLY FLUORESCENT SAMPLES												
70001	0.764	0.596	0.743	0.778	.....	0.77	0.320	0.327	.....	.....	0.316	0.328
70002	.776	.610	.755	.795	.....	.77	.329	.335	.....	.....	.322	.330
70003	.754	.599	.740	.772	.....	.74	.334	.344	.....	.....	.328	.338
70004	.650	.550	.622	.663	.....	.63	.348	.354	.....	.....	.343	.349
70005	.636	.549	.611	.634	.....	.63	.371	.376	.....	.....	.370	.376

TABLE 2.—*Summary of measurements of daylight reflectance relative to magnesium oxide, Y, and chromaticity coordinates, x and y*—Continued

A. STANDARD COLOR CARD OF AMERICA—Continued

TCCA cable number	Daylight reflectance, Y						Chromaticity coordinates, x and y					
	Multipurpose			Spectrophotometer	Macbeth Martens	Visual estimate via Munsell scales	Spectrophotometer		Subtractive colorimeter		Visual estimate via Munsell scales	
	White backing	Black backing	From eq 2				x	y	x	y	x	y
WEAKLY FLUORESCENT SAMPLES—continued												
70006	0.645	0.534	0.612	0.622		0.63	0.409	0.403			0.403	0.403
70007	.650	.545	.620	.653	0.627	.63	.305	.317			.301	.313
70008	.543	.471	.514	.550		.51	.285	.300			.286	.297
70009	.556	.470	.522	.557		.51	.281	.298			.275	.294
70010	.381	.356	.367	.405		.40	.275	.292	0.270	0.292	.267	.279
70011	.408	.375	.390	.450		.40	.267	.280	.255	.277	.267	.280
70012	.367	.338	.350	.388		.38	.243	.265	.237	.265	.240	.262
70013	.693	.571	.664	.683	.640	.65	.340	.327			.341	.328
70014	.671	.549	.638	.644		.65	.348	.319			.346	.318
70015	.603	.507	.570	.584		.59	.359	.316			.361	.321
70016	.584	.495	.552	.562	.530	.53	.362	.313			.361	.314
70017	.500	.417	.462	.466	.436	.43	.385	.309	.385	.306	.389	.309
70018	.334	.307	.317	.321		.31	.308	.310	.404	.310	.390	.310
70019	.564	.495	.538	.560		.54	.299	.323			.294	.323
70020	.484	.436	.462	.485		.49	.271	.316			.274	.323
70021	.343	.322	.330	.371		.34	.246	.298	.231	.288	.24	.29
70022	.225	.217	.219	.240		.22	.202	.262	.210	.256	.216	.269
70031	.525	.461	.498	.523		.53	.340	.377	.338	.381	.335	.376
70032	.365	.357	.360	.411		.40	.311	.371			.311	.380
70041	.169	.150	.152	.164		.16	.592	.344	.592	.338	.597	.338
70042	.134	.120	.122	.133		.134	.587	.327			.581	.323
70043	.326	.311	.316	.337		.34	.262	.274			.264	.270
70054	.040	.039	.039	.042		.046	.428	.246	.441	.246	.41	.25
70063	.148	.154	.153	.174		.16	.287	.472	.284	.500	.283	.482
70064	.080	.080	.080	.072		.080	.290	.434			.292	.435
70067	.687	.542	.649	.673		.66	.414	.424			.411	.417
70073	.157	.155	.156	.182		.18	.259	.232	.245	.218	.259	.234
70080	.163	.146	.148	.149	.136	.148	.567	.307			.556	.309
70091	.530	.476	.508	.519		.51	.366	.358			.369	.361
70097	.407	.368	.385	.382	.368	.36	.377	.298	.382	.297	.377	.303
70104	.247	.239	.241	.253	.228	.23	.368	.355			.364	.353
70109	.342	.331	.335	.340		.34	.293	.304			.295	.303
70110	.185	.182	.182	.193		.20	.286	.293			.289	.297
70115	.377	.345	.358	.374	.362	.35	.414	.389			.407	.383
70116	.328	.310	.316	.321	.284	.29	.438	.394			.428	.387
70121	.413	.383	.397	.414		.42	.283	.288			.285	.291
70122	.266	.262	.263	.280		.26	.294	.264			.269	.269
70123	.127	.125	.126	.150		.134	.253	.247	.238	.234	.247	.244
70124	.318	.296	.302	.310		.30	.300	.332	.305	.331	.385	.332
70127	.615	.532	.569	.595	.586	.56	.377	.365			.366	.358
70128	.345	.333	.337	.340	.311	.32	.389	.374			.387	.372
70135	.026	.035	.031	.040		.037	.298	.222			.302	.221
70139	.350	.329	.337	.358	.334	.35	.352	.347			.346	.343
70142	.227	.226	.226	.251		.24	.247	.275			.259	.284
70148	.573	.493	.544	.553		.52	.305	.358			.400	.359
70151	.306	.297	.300	.310		.30	.322	.325			.318	.323
70152	.283	.273	.276	.294		.30	.314	.316			.311	.312
70166	.261	.255	.257	.287		.26	.320	.401			.311	.405
70169	.300	.292	.295	.299		.30	.332	.330			.325	.324
70175	.199	.194	.195	.212		.22	.250	.269			.258	.276
70181	.511	.455	.487	.496		.47	.362	.323			.358	.323
70182	.284	.271	.275	.286	.269	.30	.383	.310			.375	.312
70183	.431	.401	.415	.433		.42	.378	.397			.378	.403
70185	.391	.370	.379	.394		.39	.325	.325			.317	.318
70187	.405	.376	.389	.403		.40	.369	.369			.365	.366
70189	.211	.202	.204	.207		.21	.356	.288	.364	.287	.363	.290
70191	.309	.296	.300	.308		.31	.383	.354			.393	.362
70193	.390	.368	.378	.384		.39	.324	.330			.324	.331
70194	.399	.368	.382	.392		.40	.372	.339	.368	.338	.366	.339
70195	.249	.240	.242	.291		.27	.285	.292			.280	.290

TABLE 2.—*Summary of measurements of daylight reflectance relative to magnesium oxide, Y, and chromaticity coordinates, x and y*—Continued

A. STANDARD COLOR CARD OF AMERICA—Continued

TCCA cable number	Daylight reflectance, Y						Chromaticity coordinates, x and y					
	Multipurpose			Spectrophotometer	Macbeth Martens	Visual estimate via Munsell scales	Spectrophotometer		Subtractive colorimeter		Visual estimate via Munsell scales	
	White backing	Black backing	From eq 2				x	y	x	y	x	y
WEAKLY FLUORESCENT SAMPLES—continued												
70196	0.394	0.366	0.378	0.390	0.358	0.38	0.398	0.394	0.403	0.399	0.397	0.397
70197	.506	.454	.484	.514	.....	.52	.313	.329	.....	.....	.313	.329
70199	.470	.416	.444	.456	.....	.43	.339	.342	.....	.....	.332	.338
70200	.386	.357	.369	.409	.....	.40	.310	.342	.302	.342	.298	.345
70201	.307	.369	.341	.400	.....	.39	.362	.350	.....	.....	.359	.347
70203	.584	.510	.558	.556	.....	.57	.412	.416	.....	.....	.422	.424
70204	.214	.212	.212	.256	.....	.24	.273	.301	.....	.....	.266	.303
70208	.513	.443	.482	.497	.....	.48	.419	.469	.419	.478	.423	.483
70209	.088	.084	.085	.108	.099	.107	.176	.170	.169	.160	.18	.18
70211	.102	.102	.102	.126	.....	.104	.217	.226	.....	.....	.217	.225
70215	.349	.326	.335	.354	.....	.34	.460	.460	.460	.470	.448	.461
70216	.033	.045	.039	.056	.....	.050	.201	.145	.193	.132	.195	.140
STRONGLY FLUORESCENT SAMPLES												
70025	0.609	0.507	0.575	0.624	0.543	0.56	0.369	0.354	0.400	0.331	0.389	0.330
70026	.557	.473	.524	.559	.513	.51	.399	.357	.416	.343	.411	.349
70027	.571	.476	.535	.598	.512	.51	.384	.368	.435	.330	.411	.341
70028	.517	.433	.480	.540	.374	.40	.405	.371	.462	.327	.434	.344
70029	.305	.276	.285	.310	.241	.26	.446	.371	.494	.231	.483	.347
70030	.214	.193	.197	.209	.171	.18	.532	.339	.556	.336	.529	.333
70037	.464	.406	.435	.453	.399	.43	.406	.375	.415	.375	.406	.368
70038	.485	.412	.450	.480	.424	.43	.440	.376	.446	.372	.432	.369
70039	.388	.342	.361	.388	.325	.31	.460	.373	.486	.354	.479	.358
70040	.200	.187	.189	.196	.161	.19	.549	.354	.549	.338	.54	.34
70049	.143	.132	.133	.141	.116	.134	.460	.263	.474	.259	.472	.263
70050	.098	.093	.093	.109	.076	.080	.496	.278	.501	.270	.47	.26
70051	.079	.077	.077	.088	.072	.075	.469	.260	.456	.260	.447	.260
70052	.060	.056	.056	.067	.048	.061	.461	.269	.486	.256	.45	.26
70053	.062	.060	.060	.069	.054	.061	.452	.262	.476	.254	.442	.256
70055	.332	.314	.320	.367	.289	.32	.308	.289	.300	.270	.304	.276
70056	.196	.187	.189	.210	.176	.20	.308	.253	.303	.245	.311	.253
70057	.173	.163	.165	.209	.161	.16	.297	.235	.286	.212	.292	.216
70058	.136	.135	.135	.167	.120	.134	.267	.208	.257	.179	.268	.197
70059	.038	.037	.037	.054	.033	.046	.245	.145	.227	.131	.248	.156
70072	.239	.209	.216	.224	.192	.21	.568	.369	.574	.361	.595	.380
70074	.102	.100	.100	.135	.099	.120	.247	.204	.217	.169	.243	.202
70079	.237	.205	.212	.239	.190	.21	.481	.323	.518	.296	.466	.304
70081	.091	.084	.084	.087	.075	.090	.552	.298	.552	.298	.510	.298
70082	.055	.054	.054	.055	.045	.057	.513	.284	.507	.286	.459	.287
70083	.037	.036	.036	.039	.030	.043	.460	.293	.447	.288	.435	.290
70084	.035	.034	.034	.036	.031	.046	.405	.290	.399	.289	.401	.294
70098	.265	.243	.249	.253	.231	.23	.417	.293	.426	.290	.420	.296
70099	.165	.159	.160	.190	.137	.141	.424	.293	.424	.281	.416	.285
70100	.085	.085	.085	.100	.079	.075	.429	.280	.436	.269	.424	.271
70101	.031	.029	.029	.041	.025	.035	.420	.298	.389	.280	.387	.283
70103	.358	.342	.348	.343	.332	.33	.374	.347	.354	.355	.357	.357
70118	.144	.142	.142	.147	.145	.16	.461	.383	.467	.379	.460	.384
70126	.048	.046	.046	.058	.046	.057	.455	.336	.441	.327	.421	.328
70133	.439	.410	.424	.483	.406	.40	.310	.289	.311	.274	.314	.270
70149	.326	.290	.302	.317	.282	.29	.482	.358	.500	.346	.487	.350
70150	.134	.127	.128	.133	.112	.130	.514	.335	.528	.336	.495	.330
70160	.199	.187	.189	.191	.173	.18	.506	.374	.519	.377	.499	.369
70161	.087	.086	.086	.088	.077	.090	.515	.357	.517	.355	.491	.359
70162	.083	.081	.081	.097	.069	.085	.473	.361	.474	.346	.467	.346

TABLE 2.—*Summary of measurements of daylight reflectance relative to magnesium oxide, Y, and chromaticity coordinates, x and y*—Continued

A. STANDARD COLOR CARD OF AMERICA—Continued

TCCA cable number	Daylight reflectance, Y						Chromaticity coordinates, x and y					
	Multipurpose			Spectrophotometer	Macbeth Martens	Visual estimate via Munsell scales	Spectrophotometer		Subtractive colorimeter		Visual estimate via Munsell scales	
	White backing	Black backing	From eq 2				x	y	x	y	x	y
STRONGLY FLUORESCENT SAMPLES—continued												
70172	0.091	0.089	0.089	0.105	0.086	0.090	0.338	0.193	0.324	0.179	0.328	0.187
70173	.053	.050	.050	.061	.046	.053	.315	.174	.294	.158	.31	.17
70174	.048	.046	.046	.055	.042	.050	.316	.191	.305	.182	.309	.197
70178	.323	.288	.300	.320	.290	.31	.463	.345	.484	.317	.457	.329
70179	.152	.138	.140	.138	.131	.134	.569	.308	.568	.309	.556	.313
70180	.084	.079	.080	.080	.070	.085	.600	.305	.590	.307	.550	.310
70184	.096	.096	.096	.118	.086	.107	.405	.388	.398	.390	.387	.387
70202	.381	.356	.367	.381	.329	.32	.329	.279	.324	.270	.336	.267
70205	.581	.508	.556	.578	.592	.63	.409	.404	.427	.446	.428	.452
70206	.469	.392	.431	.458	.439	.43	.414	.339	.428	.314	.42	.32
70207	.205	.201	.202	.236	.221	.22	.238	.294	.218	.297	.222	.296
70210	.150	.134	.136	.147	.114	.130	.516	.289	.549	.284	.492	.284
70212	.117	.117	.117	.147	.120	.130	.270	.205	.251	.181	.263	.199
70213	.136	.121	.123	.143	.118	.134	.367	.200	.408	.190	.392	.216
70214	.252	.239	.242	.304	.291	.29	.269	.408	.254	.424	.253	.405

B. UNITED STATES ARMY COLOR CARD

TCCA cable number	Daylight reflectance, Y				Chromaticity coordinates, x and y					
	Multipurpose	Spectrophotometer	Macbeth-Martens	Visual estimate via Munsell scales	Spectrophotometer		Subtractive colorimeter		Visual estimate via Munsell scales	
					x	y	x	y	x	y
NONFLUORESCENT SAMPLES										
65001	0.436	0.462	----------	0.43	0.475	0.459	0.479	0.461	0.458	0.453
65005	.641	.713	----------	.66	.328	.335	.330	.336	.327	.335
65007	.077	.078	----------	.085	.295	.408	.293	.412	.294	.402
65008	.285	.333	----------	.30	.319	.325	.319	.324	.318	.325
65009	.055	.062	----------	.059	.252	.169	.236	.151	.26	.18
65010	.048	.054	----------	.050	.181	.132	.170	.109	.184	.141
65011	.044	.047	----------	.040	.227	.201	.225	.195	.230	.207
65012	.029	.025	----------	.026	.300	.299	.301	.305	.306	.308
65014	.222	.246	----------	.22	.268	.288	.260	.285	.273	.290
65015	.440	.496	----------	.45	.394	.379	.404	.386	.395	.382
65018	.029	.025	----------	.026	.302	.304	.307	.314	.309	.312
65019	.044	.039	----------	.040	.230	.221	.235	.225	.224	.217
65020	.066	.061	----------	.080	.529	.326	.516	.328	.502	.329
65021	.372	.414	----------	.39	.426	.428	.427	.431	.429	.428
65022	.194	.212	----------	.21	.364	.448	.363	.445	.363	.454
WEAKLY FLUORESCENT SAMPLES										
65002	0.406	0.422	----------	0.39	0.507	0.438	0.521	0.442	0.491	0.428
65006	.109	.096	----------	.101	.556	.318	.564	.322	.54	.32
65016	.074	.070	----------	.080	.424	.366	.422	.367	.420	.364
65017	.044	.043	----------	.043	.386	.307	.385	.306	.398	.309
STRONGLY FLUORESCENT SAMPLES										
65003	0.342	0.350	0.316	0.31	0.502	0.413	0.518	0.402	0.505	0.401
65004	.250	.258	.212	.20	.541	.377	.572	.363	.55	.36
65013	.104	.098	.083	.085	.483	.275	.503	.272	.465	.276

Table 3 shows the degree of agreement of the spectrophotometric determinations of chromaticity differences (Δx, Δy) between samples of the standard card having neighboring chromaticities with the determination of the same differences by means of the subtractive, or chromaticity-difference, colorimeter. These cross-checks were carried out wherever possible to evaluate the importance of the known sources of error and to detect any unsuspected sources which might have affected the results. Every sample that was not cross-checked in this way was compared to some other known color standard, chiefly with one of the Munsell standards; see tables 2, A, and 2, B.

TABLE 3.—*Agreement of the spectrophotometric determinations of chromaticity differences (Δx, Δy) between neighboring samples of the Standard Card with the determination of the same differences by the subtractive colorimeter*

Nonfluorescent pairs			Pairs involving only weakly and nonfluorescent samples			Pairs involving strongly fluorescent samples		
TCCA cable numbers	Discrepancy in—		TCCA cable numbers	Discrepancy in—		TCCA cable numbers	Discrepancy in—	
	Δx	Δy		Δx	Δy		Δx	Δy
70023, 70024	0.005	0.004	70001, 70002	0.001	0.001	70025, 70026	0.014	0.010
70034, 70130	.009	.004	70002, 70003	.002	.002	70027, 70028	.005	.007
70034, 70035	.000	.000	70003, 70004	.001	.001	70029, 70149	.030	.033
70036, 70066	.003	.003	70004, 70005	.004	.003	70030, 70150	.048	.004
70044, 70143	.002	.001	70006, 70203	.001	.000	70037, 70038	.003	.003
70046, 70144	.001	.001	70007, 70008	.005	.005	70039, 70149	.008	.006
70047, 70048	.007	.003	70008, 70009	.000	.000	70049, 70050	.011	.004
70062, 70061	.009	.003	70010, 70011	.007	.003	70051, 70050	.015	.009
70069, 70070	.001	.002	70011, 70012	.006	.004	70052, 70053	.002	.005
70071, 70070	.006	.001	70013, 70014	.001	.001	70054, 70053	.011	.008
70075, 70076	.004	.004	70015, 70016	.000	.001	70056, 70057	.012	.021
70077, 70078	.002	.006	70017, 70097	.006	.002	70058, 70057	.006	.000
70085, 70086	.004	.003	70018, 70017	.007	.002	70072, 70040	.006	.008
70087, 70086	.002	.000	70019, 70020	.004	.003	70081, 70180	.012	.002
70088, 70089	.004	.006	70032, 70197	.003	.002	70082, 70083	.007	.006
70090, 70114	.002	.005	70033, 70032	.001	.000	70084, 70083	.007	.004
70093, 70092	.002	.001	70064, 70065	.009	.001	70099, 70098	.009	.010
70094, 70140	.002	.002	70067, 70203	.003	.000	70101, 70190	.027	.023
70095, 70119	.003	.001	70080, 70042	.003	.005	70102, 70101	.033	.018
70095, 70141	.001	.001	70104, 70105	.001	.001	70118, 70117	.004	.001
70096, 70108	.003	.006	70109, 70195	.011	.004	70133, 70055	.010	.004
70106, 70105	.003	.002	70110, 70195	.008	.003	70134, 70057	.011	.023
70107, 70095	.001	.003	70115, 70128	.002	.002	70148, 70038	.002	.003
70108, 70107	.001	.000	70116, 70115	.010	.002	70161, 70162	.002	.013
70111, 70112	.002	.001	70121, 70122	.002	.002	70172, 70173	.006	.001
70113, 70112	.005	.004	70122, 70043	.004	.000	70173, 70174	.010	.006
70120, 70095	.004	.003	70127, 70091	.001	.000	70178, 70206	.007	.004
70129, 70117	.002	.001	70135, 70164	.000	.006	70179, 70080	.001	.001
70131, 70130	.000	.001	70142, 70175	.002	.002	70184, 70159	.007	.002
70132, 70066	.000	.001	70145, 70020	.005	.004	70188, 70103	.020	.008
70137, 70138	.000	.002	70146, 70204	.003	.003	70198, 70098	.000	.001
70143, 70045	.008	.005	70152, 70151	.001	.001	70202, 70133	.007	.007
70155, 70154	.008	.002	70153, 70152	.005	.001	70212, 70058	.011	.001
70158, 70157	.002	.002	70169, 70185	.001	.001			
70168, 70167	.003	.009	70170, 70152	.002	.002			
70171, 70186	.002	.002	70181, 70015	.000	.000			
70176, 70177	.000	.002	70182, 70097	.004	.003			
			70183, 70031	.012	.004			
			70187, 70005	.004	.001			
			70191, 70092	.001	.001			
			70193, 70136	.002	.001			
			70199, 70136	.000	.001			
			70201, 70045	.005	.003			
			70201, 70139	.004	.002			
Averages	0.003	0.003	Averages	0.004	0.002	Averages	0.011	0.007

Every sample of the official copy of the standard card was compared visually with the corresponding unmounted sample, and for 134 of the 216 colors noticeable differences could be discerned. Eight of these differences were considered large enough to warrant evaluation and Munsell book notations of the corresponding unmounted samples were found by one observer (GBR) for comparison with those already found for the mounted samples. This comparison is given in table 4. As these samples are cut from the same piece of fabric and from the same dyeing, these differences must be due to a fugitive character of the dyestuff itself. Elsewhere in this paper the results refer to the unmounted samples supplied especially for this study.

TABLE 4.—*Munsell book notations for 8 colors for which the differences between the mounted and unmounted samples were considered large enough to warrant evaluation*

TCCA cable number	Munsell book notation	
	Mounted	Unmounted
70008	2.0PB 7.5/2.5	1.5PB 7.5/2.5
70021	2.0B 6.2/5.5	2.0B 6.3/6.0
70055	7.0P 6.1/2.8	6.5P 6.1/3.5
70073	9.5PB 4.6/5.5	9.0PB 4.6/6.0
70074	8.5PB 4.0/7.0	9.5PB 3.9/8.0
70187	2.5Y 6.8/3.2	2.0Y 6.9/3.2
70200	2.5G 6.6/2.0	2.5G 6.7/2.2
70204	10.0BG 5.2/2.4	1.0B 5.3/2.8

V. DISCUSSION

From columns 2 and 3 of table 2,A, it may be seen that generally, as should be expected, the daylight reflectance of the sample with a white backing was found to be higher than that with a black backing. None of the reversals exceed 0.007, and it is reasonable to ascribe them to a greater or less bulging of the sample into the reflectometer, which it was impossible to avoid.

Column 4 of table 2,A, contains the reflectances for two layers of the samples backed by white paper computed by eq 2. Comparison of these reflectances with those obtained for the nonfluorescent samples from reduction of the spectrophotometric data (column 5) reveals a fairly consistent tendency of the former to be lower by about 0.010. The difference is ascribed to the acceptance by the spectrophotometer (nearly normal illumination, nearly diffuse viewing) of a greater proportion of the surface-reflected light from these samples than was accepted by the multipurpose reflectometer (approximately 45° illumination, normal viewing). If the spectrophotometric data were not available, it may be seen that a fairly reliable indication of what would be obtained spectrophotometrically on nonfluorescent and weakly fluorescent samples of this material and weave is given by adding 0.010 to the reflectances in column 4. The adopted values in section VI for the nonfluorescent and weakly fluorescent samples are therefore found by adding 0.010 to the values obtained by the multipurpose reflectometer (column 4) and averaging with the spectrophotometric daylight reflectances (column 5).

The validity of this procedure was checked by measurements of daylight reflectance of 15 weakly fluorescent samples by comparison

with Munsell standards by way of the Macbeth-Martens reflectometer; see table 2,A, column 6. The results of these measurements are lower than the adopted values by fairly consistent amounts, both for the five nonfluorescent samples and for the 15 weakly fluorescent samples. By comparison of five Munsell neutrals with five nearly neutral nonfluorescent samples of the standard card both on the Macbeth-Martens reflectometer and under the angular conditions (nearly diffuse-normal) of the recording spectrophotometer, it was shown that the Macbeth-Martens reflectometer read lower on the textile samples by an average amount of 0.011. Remaining discrepancies in table 2,A, of about 0.010 are unexplained, but are ascribable in part to failure of the Munsell standards used to agree exactly with the published specifications.

Column 7 of table 2, A, gives estimates of the daylight reflectances obtained by way of Munsell notations found by comparing the textile samples with the charts of the Munsell Book of Color. These estimates serve as a closing check on errors of all sorts. It will be noted that the agreement is generally good. These visual estimates also serve to indicate whether to correct the spectrophotometric measurements by subtracting 0.010 or 0.011 as a correction for specularly reflected light included in the measurement, or whether to correct the multipurpose-reflectometer results by adding 0.010 and the Macbeth-Martens results by adding 0.011 (as was actually done). The visual estimates for the standard card were found to agree on the average with the spectrophotometric results of daylight reflectance. It was concluded that the conditions of normal illumination with nearly diffuse viewing accords with viewing near a window more closely than does the 45°-normal condition for these textile samples. Corrections accordingly were applied to the 45°-normal results. This procedure assures that the adopted reflectances will be in agreement with comparisons to the Munsell standards carried out in the customary way.

From the cross-checks of table 3 it may be seen that the spectrophotometer and the colorimeter agree for the nonfluorescent pairs and for the pairs involving only weakly and nonfluorescent samples on the average within about 0.003 in x or y. The maximum difference found for these samples is 0.012. But pairs involving one or more strongly fluorescent samples sometimes yield discrepancies of more than 0.020. Although the chromaticity coordinates (x,y) do not yield scales of uniform perceptibility, it may be safely stated that a difference equal to 0.001 in x or y within the range of these samples is definitely detectable by means of the chromaticity-difference colorimeter. Many of the cross-checks therefore reveal discrepancies much too large to be ascribed to experimental uncertainty.

Analysis of the chromaticity data of tables 2, A and B, by plotting the spectrophotometric results on the (x,y)-diagram, together with the results by means of the chromaticity-difference, or subtractive, colorimeter and by visual estimate also indicates many discrepancies too large to ascribe to experimental error of setting the colorimeter. On this account, studies were made of the various sources of such discrepancies. These sources were found to be (a) variations in angular conditions of illuminating and viewing the samples, (b) metamerism, or differences in spectral character of two samples of similar color, (c) fluorescence, and (d) uncertainties in estimation of Munsell book notation.

1. ANGULAR CONDITIONS

One of the possible reasons why the spectrophotometric result and the colorimetric result should fail to agree with each other and with the visual estimates is the disparity in angular conditions. From an analysis of the reflectance data it was found that the nearly normal-diffuse angular conditions of the recording spectrophotometers used have caused the daylight reflectances derived therefrom to be higher on the average by about 0.010 than those found by use of 45°-normal angular conditions. This regular disparity is ascribed to the greater proportion of surface-reflected light accepted for measurement by the spectrophotometer, and as this surface-reflected light is spectrally very similar to the illuminant, it would be expected that the chromaticity points found by comparison with the considerably less glossy Munsell standards by way of the chromaticity-difference colorimeter (approximately normal-45° angular conditions) would be generally further on the (x,y)-diagram from the illuminant point than the corresponding chromaticity points evaluated by way of the spectrophotometer. Furthermore, it is to be expected from the analysis of reflectance results, that the same disparity would be found between the colorimeter results and those by visual estimate.

Analysis of the chromaticity data of tables 2, A and B, have borne out this expectation to a very satisfactory degree. For graphical comparison therefore, the colorimetric results have been adjusted to accord with addition of a specular component equal to 0.010 as follows:

$$\begin{aligned} X_a &= X + 0.010 X_0, \\ Y_a &= Y + 0.010 Y_0, \\ Z_a &= Z + 0.010 Z_0, \end{aligned} \tag{4}$$

where Y is the daylight reflectance relative to magnesium oxide determined for 45°-normal angular conditions, X and Z are found from the chromaticity coordinates (x,y,z) determined by comparison with the Munsell standards under normal-45° angular conditions by eq 4a:

$$\begin{aligned} X &= Y(x/y), \\ Z &= Y(z/y) = Y(1-x-y)/y, \end{aligned} \tag{4a}$$

and X_0, Y_0, Z_0 are the tristimulus values for the illuminant, in this case, ICI standard illuminant C [9, 15, 28], which corresponds to $X_0=0.980$, $Y_0=1.000$, $Z_0=1.181$. The adjusted chromaticity coordinates (x_a,y_a) are found in the usual way by eq 4b:

$$x_a = X_a/(X_a+Y_a+Z_a),\ y_a = Y_a/(X_a+Y_a+Z_a). \tag{4b}$$

Figure 3 shows on the (x, y)-chromaticity diagram a comparison of the chromaticities of a number of nonfluorescent and weakly fluorescent samples of the standard card found (circles) by way of the spectrophotometer, (dots) by chromaticity-difference colorimeter comparisons with the Munsell standards adjusted by eq 4 to correspond to more surface-reflected light, and (triangles) by visual estimate along the scales of the Munsell Book of Color. It will be noted that the major discrepancies occur along lines which would nearly intersect the illuminant point (C), that is, along lines close to those of constant

dominant wavelength [27]. These discrepancies are ascribed partly to uncertainty in the zero-adjustment of the recording spectrophotometer and partly to small differences in luster between the various textile samples which make one single adjustment as by eq 4 not perfectly adequate. The differences ascribable to these causes are estimated as less than 0.010 in x or y, except for the very dark chromatic samples (such as 70060, 70066, 70075, 70088, and 70165).

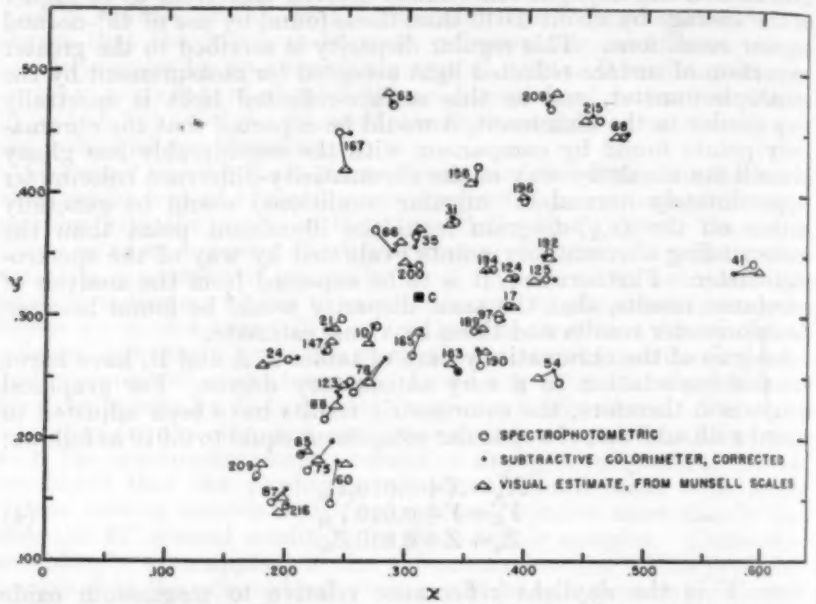


FIGURE 3.—*Chromaticities of a number of nonfluorescent and weakly fluorescent samples of the Standard Color Card of America obtained by three different methods (see text).*

The major portion of the discrepancies indicated occur along straight lines which, if extended, would pass close to the illuminant point (*C*).

There are also minor deviations in dominant wavelength, which are generally erratic and ascribable to experimental error, except for certain colors of orange-red hue. The visual estimates for these samples (see 70026, 70028, 70029, and 70072 in fig. 5; also 70027, 70039, 70149, and 70178, not shown) deviate toward orange from the dominant wavelength of the adopted values. These deviations would be explained if the highlights resulted from a combination of the purely surface-reflected light with an appreciable component which had penetrated one or two fiber layers, thus acquiring the more orange characteristic of the same dye applied in a lower concentration, or strength, and it is likely that this is the correct explanation. This conjecture has not been subjected to experimental verification.

2. METAMERISM

Two samples form a metameric pair if they are visually identical or nearly identical and at the same time spectrally considerably different. In a study of the cross-checks given in table 3, it was found that a somewhat greater discrepancy may be expected for highly metameric

pairs than for pairs showing little or no metamerism. Figure 4 shows the spectral-reflectance curves of four nonfluorescent samples (70034, 70035, 70130, 70131) of the standard card. Samples 70034 and 70035 correspond to the same or similar dye mixtures with some difference in strength of the dyeing, and the same remark applies to 70130 and 70131. Table 3 shows a virtually perfect cross-check for these two nearly nonmetameric pairs. Samples 70034 and 70130,

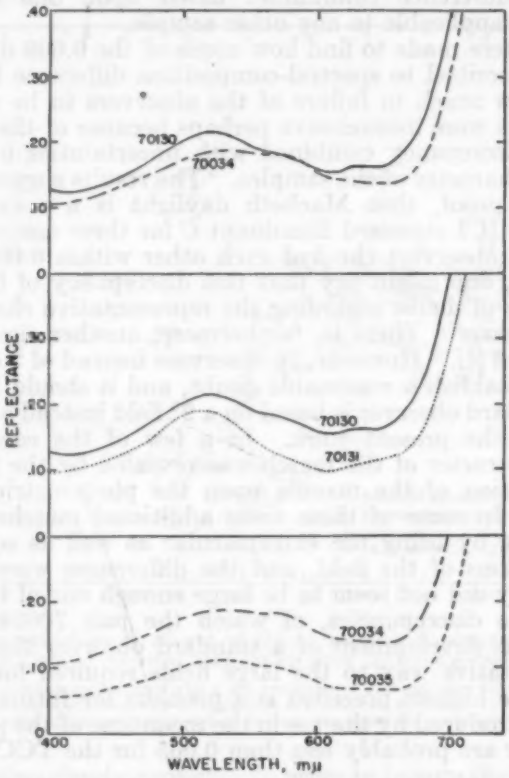


FIGURE 4.—*Spectral-reflectance curves of a metameric pair (70130, 70034) of samples and of two pairs, (70130, 70131) and (70034, 70035), that are nearly nonmetameric.*

The cross-check of the first pair revealed a discrepancy of 0.009 in chromaticity coordinates (*x*,*y*); those of the other two, 0.001 and 0.000, respectively.

however, form a metameric pair; they have nearly the same color but show a considerable difference in shape of spectrophotometric curve. Table 3 also shows that Δx for this pair obtained by the spectrophotometer differs from that by the subtractive colorimeter by 0.009, and the corresponding discrepancy in Δy is 0.004. This study suggests that differences in spectral composition of a degree to cause uncertainty of about 0.010 in chromaticity coordinates (x,y) may be frequently encountered in textile dyeings. It is likely that other similar discrepancies among the nonfluorescent and weakly fluorescent samples listed in table 3 have the same explanation.

Metamerism of the various pairs influences these comparisons (1) because of difference between the illumination used in reducing the

spectrophotometric data (ICI standard illuminant *C*) and that effective in comparisons by means of the chromaticity-difference colorimeter (Macbeth daylight), and (2) because of difference in spectral sensitivity of the observers, the standard ICI observer being used to reduce the spectrophotometric data, and one or two normal but somewhat nonstandard observers being used to obtain the colorimetric comparisons. Metamerism also prevents calibration of the chromaticity-difference colorimeter based upon one sample from being strictly applicable to any other sample.

Attempts were made to find how much of the 0.009 discrepancy in x should be ascribed to spectral-composition difference in the illuminant, and how much to failure of the observers to be nonstandard; but the results were inconclusive perhaps because of the rather small size of the discrepancy combined with uncertainties introduced by the lustrous character of the samples. The results suggested, without being actual proof, that Macbeth daylight is a very satisfactory substitute for ICI standard illuminant *C* for these comparisons.

As the two observers checked each other within 0.003 in x and y in every trial, one might say that this discrepancy of 0.009 raises a certain degree of doubt regarding the representative character of the standard observer. There is, furthermore, another similar disagreement on record [4]. However, 20 observers instead of 2 or 3 would be required to establish a reasonable doubt, and it should be noted also that the standard observer is based on a 2° field instead of the 9 by 13° field used in the present work. In a few of the comparisons the metameric character of the match was revealed by the presence of a visible projection of the macula upon the photometric field of the colorimeter. In some of these cases additional matches were made with difficulty by using the extramacular as well as some with the macular portions of the field, and the differences were appreciable. However, they did not seem to be large enough nor of the right kind to resolve the discrepancies, of which the pair 70034–70130 is an example. The development of a standard observer that shall apply in a representative way to the large fields required for colorimetric settings of the highest precision is a problem for future study. Uncertainties introduced by the use in the meantime of the present standard observer are probably less than 0.005 for the TCCA samples.

3. FLUORESCENCE

Figure 5 shows comparisons of chromaticities similar to those of figure 3 but with reference to strongly fluorescent samples. Of the 55 strongly fluorescent samples of the standard card, only 33 are represented in figure 5, the remaining 22 being omitted for the sake of clarity and because they show discrepancies very similar to those which are represented. It will be noted that a large number of the strongly fluorescent samples have caused the spectrophotometer to yield a significantly wrong result. For strongly fluorescent samples the adopted values are based upon the adjusted results from the chromaticity-difference colorimeter and the Macbeth-Martens reflectometer, with no weight given either to the spectrophotometric result or to those by the multipurpose reflectometer.

Although the cross-checks summarized in table 3 for pairs including strongly fluorescent samples serve to reveal most of the corresponding

errors arising from fluorescence, they do not invariably reveal them. See, for example, the good check obtained by comparing 70037 with 70038. The spectrophotometric evaluation of the difference in x and y between these two samples agrees with that by the chromaticity-difference colorimeter within 0.003. These two samples are fluorescent to about the same extent and in about the same way. Each sample is evaluated by routine application of the recording spectrophotometer with closely the same error, the difference between these erroneous

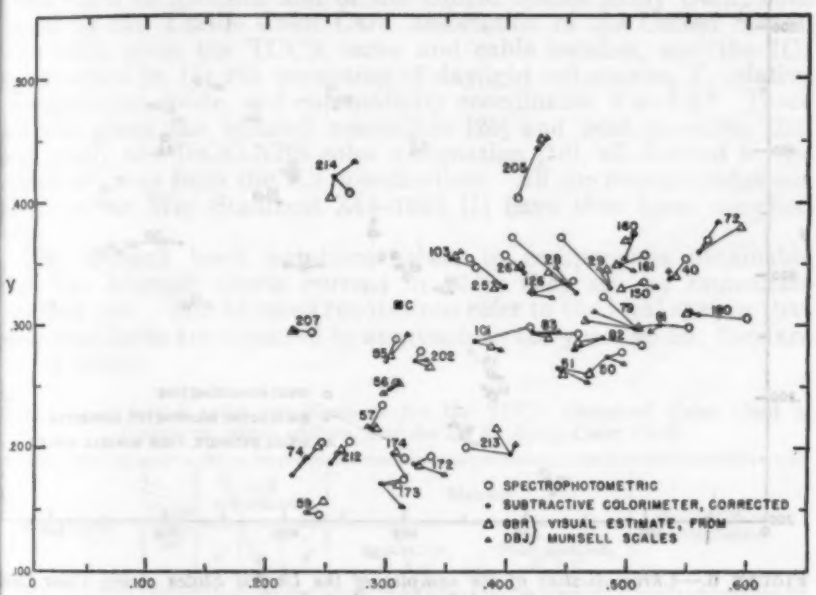


FIGURE 5.—*Chromaticities of 53 out of the 55 strongly fluorescent samples of the Standard Color Card of America obtained by three different methods (see text).*

Note that the spectrophotometric result for a large number of these samples differs importantly from those by the other two methods known to be applicable to fluorescent samples. It is therefore presumed that the degree and kind of fluorescence is such as to make the recording spectrophotometer inapplicable to these samples.

evaluations being closely correct. In order to be sure that an unknown sample is not too strongly fluorescent to prevent reliable use of the spectrophotometer, the cross-check must involve one nonfluorescent sample. The spectrophotometric evaluation of some of these strongly fluorescent samples is in error by more than 0.020 in x or y. However, the adopted values are considered to be uncertain by less than 0.005 from this cause.

4. MUNSELL BOOK NOTATIONS

In figures 3 and 5 and in figure 6, which shows a similar plot for the samples of the Army card, it will be noted that the visual estimates of chromaticity coordinates, x and y, found by interpolation and extrapolation along the scales of the Munsell Book of Color, with a few exceptions agree well with corrected values from the chromaticity-difference colorimeter and with the spectrophotometric values for nonfluorescent and weakly fluorescent samples. As many of these estimates involve extrapolation of two kinds, first to find the Munsell

book notation by extrapolation along the color scales, and, finally, to estimate the corresponding chromaticity coordinates by extrapolation on large-scale (x,y)-plots, the chromaticity coordinates of the 55 strongly fluorescent samples were estimated independently by a second observer (DBJ). Some of these are plotted on figure 5 (small triangles), and it may be seen that the discrepancies are considerable

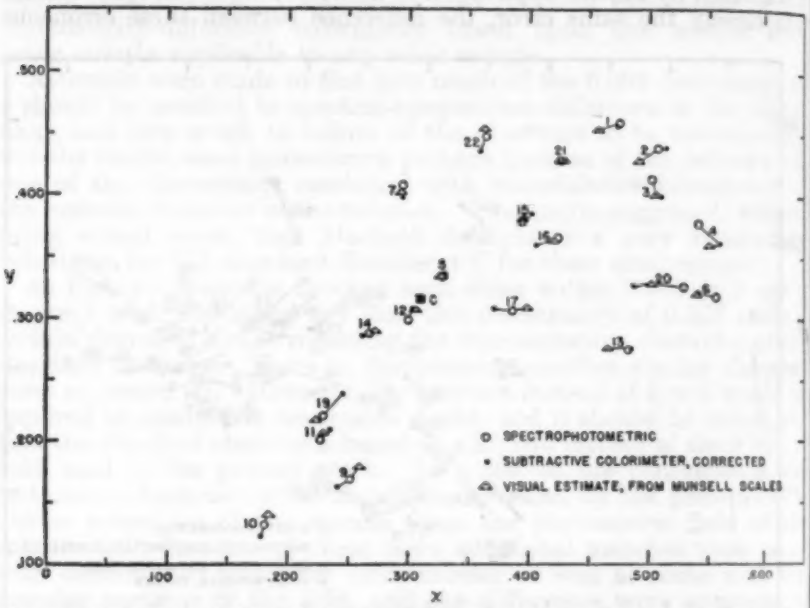


FIGURE 6.—*Chromaticities of the samples of the United States Army Color Card by three different methods (see text).*

Three of the samples (65003, 65004, and 65013) are strongly fluorescent (see table 2, B); the spectrophotometric results for these samples should not be expected to agree well with those by the other two methods.

for some samples (70050, 70172, 70173, 70213, and 70214). These discrepancies give an indication of the uncertainty ascribable partly to the texture difference but chiefly to extrapolation, and because of this uncertainty, the adopted values of Munsell book notation are given only to the nearest hue step or chroma step if extrapolation of more than one chroma step is involved.

From the rather large fraction (52/238) of these textile standards that can be given Munsell book notations only by extrapolation of considerable extent it may be seen that the TCCA standards cover color ranges somewhat beyond those covered by the matte, evenly spaced nonfluorescent Munsell standards. This increase in color range has been achieved by using dyes (some of them fluorescent) instead of pigments, and by making no sacrifice of purity for the sake of uniform spacing. Most of these TCCA standards are also outside the range covered by the Jacobson-Foss Color Harmony Manual [8]. As the colors represented are those for which there has been demonstrated to be a continuing demand, and as no other calibrated set of material color standards covers this range fully, it may be seen that the TCCA standards fill an important and unique need. This need is not confined to textiles alone but relates also to this extended

color range procurable with fluorescent colorants in any medium (paints, plastics, ceramics).

VI. FUNDAMENTAL SPECIFICATION OF THE TEXTILE COLOR CARD ASSOCIATION STANDARDS

Table 5 shows the adopted color specifications of the Standard Color Card of America and of the United States Army Card, both issued by the Textile Color Card Association of the United States. This table gives the TCCA name and cable number, and the ICI specification [9, 15, 28], consisting of daylight reflectance, Y, relative to magnesium oxide, and chromaticity coordinates x and y.[3] There are also given the Munsell renotation [26] and book notation [25], and finally the ISCC-NBS color designation [18], all derived in the customary way from the ICI specification. All the recommendations of American War Standard Z44–1942 [1] have thus been complied with.

The Munsell book notations relate to comparisons obtainable with the Munsell charts current in 1945; they are for immediate practical use. The Munsell renotations refer to the ideal system that these standards are expected to approach as the years go on; they are for the future.

TABLE 5.—*Adopted color specifications for the TCCA Standard Color Card of American, ninth edition, and the U. S. Army Color Card*

TCCA name	Cable number	ICI specification			Munsell		ISCC-NBS color designation
		Y	*x*	*y*	Renotation, *H V/C*	Book notation, *H V/C*	
STANDARD COLOR CARD OF AMERICA							
White	70001	0.753	0.320	0.327	2.5Y 8.8/0.7	2.5Y 9.1/0.7	Yellowish white.
Ivory	70002	.765	.329	.335	1.0Y 8.9/1.3	2Y 9.1/1.6	Very pale orange.
Cream	70003	.750	.334	.344	3.5Y 8.8/1.7	4.0Y 9.1/2.2	Pale yellow.
Eggshell	70004	.632	.348	.354	1.6Y 8.2/2.5	2.3Y 8.3/3.1	Weak yellowish orange.
Leghorn	70005	.621	.371	.376	2.4Y 8.2/4.2	2.5Y 8.3/4.8	Do.
Maize	70006	.622	.409	.403	1.1Y 8.2/6.8	1.0Y 8.2/7.4	Moderate yellowish orange.
Pale Blue	70007	.634	.305	.317	8.4BG 8.2/0.5	8B 8.2/0.7	Light bluish gray.
Pastel Blue	70008	.524	.285	.300	0.2PB 7.6/2.6	9.6B 7.6/2.2	Very pale blue.
Baby Blue	70009	.532	.281	.298	.2PB 7.7/3.0	10.0B 7.6/2.8	Do.
Sky Blue	70010	.377	.273	.292	9.4B 6.6/3.4	9.0B 6.4/3.0	Pale blue.
Blue Flower	70011	.400	.262	.279	1.2PB 6.8/4.7	1.2PB 6.7/4.6	Do.
Forget-me-not	70012	.360	.241	.265	0.2PB 6.5/6.4	0.7PB 6.3/6.9	Light blue.
Flesh Pink	70013	.662	.340	.327	9.9R 8.4/2.6	9R 8.5/2	Pale to weak pink.
Baby Pink	70014	.648	.348	.319	3.4R 8.3/4.1	6R 8.5/5	Light to moderate pink.
Pastel Pink	70015	.580	.359	.316	2.0R 7.9/5.4	5R 7.9/6	Moderate pink.
Arbutus Pink	70016	.552	.362	.313	1.0R 7.8/5.9	4R 7.7/7	Moderate to strong pink.
Rose Pink	70017	.459	.384	.308	0.2R 7.2/7.9	2.2R 7.2/10.2	Strong pink.
Sea Pink	70018	.327	.400	.310	1.5R 6.2/8.2	2.5R 6.2/9.4	Light purplish red.
Tourmaline	70019	.548	.299	.323	3.4BG 7.8/1.3	7BG 7.7/1.3	Light bluish gray.
Turquoise	70020	.472	.271	.316	8.5BG 7.3/3.7	7.5BG 7.1/4.1	Light blue green.

[3] Mention should be made of the Dictionary of Colour Standards issued together with ICI specifications in 1938 by the British Colour Council, an organization based on the Textile Color Card Association and patterned after it. The published color specifications [2] are not comparable to those of the present study, first because the shiny portion of the fabric was measured rather than the ribbed, and second, because ICI standard illuminant *B* was used instead of illuminant *C*.

TABLE 5.—*Adopted color specifications for the TCCA Standard Color Card of America, ninth edition, and the U. S. Army Color Card*—Continued

TCCA name	Cable number	ICI specification			Munsell		ISCC-NBS color designation
		Y	*x*	*y*	Renotation, *H V/C*	Book notation, *H V/C*	
STANDARD COLOR CARD OF AMERICA—Continued							
Blue Turquoise	70021	0.340	0.239	0.293	2.7B 6.3/5.6	1.9B 6.2/6.0	Light greenish blue.
Grotto Blue	70022	.229	.207	.260	5.1B 5.3/7.4	5.3B 5.2/6.7	Moderate blue.
Peacock	70023	.106	.199	.257	4.2B 3.8/6.0	3.2B 3.6/6.6	Moderate greenish blue.
Duckling	70024	.052	.205	.264	2.9B 2.7/4.5	4B 2.4/5	Dusky to dark blue.
Tea Rose	70025	.554	.308	.331	6.2R 7.8/7.4	9R 7.9/9	Strong pink.
Salmon Pink	70026	.524	.414	.343	8.5R 7.6/7.7	10R 7.7/9	Strong orange pink.
Shell Pink	70027	.523	.432	.330	5.6R 7.6/10.1	8R 7.6/10	Strong pink.
Melon Pink	70028	.385	.458	.326	5.1R 6.7/11.5	7R 6.7/10	Light reddish orange.
Tigerlily	70029	.252	.486	.330	5.9R 5.6/11.3	7R 5.7/11	Moderate to strong reddish orange.
Flame Red	70030	.182	.542	.335	7.3R 4.8/12.7	6.7R 4.9/12.6	Strong reddish orange.
Nile	70031	.508	.339	.378	4.9GY 7.5/3.3	3.9GY 7.5/3.4	Pale to weak yellow green.
Pistache	70032	.370	.311	.371	0.4G 6.6/3.6	10.0GY 6.5/3.3	Weak yellowish green.
Tarragon	70033	.228	.305	.370	1.1G 5.3/3.4	1.2G 5.3/2.9	Weak green.
Palmetto	70034	.171	.315	.355	8.7GY 4.7/2.0	9GY 4.6/1.8	Dusky yellow green.
Reseda	70035	.092	.306	.361	0.8G 3.5/2.3	1G 3.2/1.7	Dusky green.
Evergreen	70036	.046	.302	.377	.6G 2.5/2.8	1.0G 2.0/2.5	Very dusky green.
Apricot	70037	.410	.412	.374	5.5YR 6.9/6.1	6.4YR 7.0/6.1	Weak orange.
Honeydew	70038	.435	.442	.370	2.5YR 7.0/8.3	2.4YR 7.2/9.0	Moderate orange.
Salmon	70039	.336	.480	.353	8.8R 6.3/10.7	9.0R 6.2/11.2	Strong reddish orange.
Tangerine	70040	.172	.538	.337	7.4R 4.7/11.9	7.0R 4.8/12.2	Do.
Paprica	70041	.162	.583	.340	8.2R 4.6/14.3	7.5R 4.5/15	Vivid reddish orange.
Pimento	70042	.132	.587	.327	7.2R 4.2/14.1	6R 4.0/15	Vivid red.
Sistine	70043	.326	.262	.273	2.6PB 6.2/4.7	2.5PB 5.9/4.1	Pale blue.
Copenhagen	70044	.158	.249	.254	4.2PB 4.5/4.8	4.3PB 4.3/4.7	Weak purplish blue.
Tile Blue	70045	.121	.239	.250	2.5PB 4.0/4.7	2.0PB 3.9/4.7	Weak blue.
Flemish Blue	70046	.078	.231	.235	3.7PB 3.3/4.7	3.6PB 3.1/4.7	Weak purplish blue.
Peking Blue	70047	.063	.214	.215	4.0PB 3.6/5.5	4.1PB 2.8/5.9	Moderate purplish blue.
Marine Corps	70048	.046	.227	.221	4.9PB 2.5/4.4	5.4PB 2.3/4.0	Dusky purplish blue.
Cherry	70049	.127	.464	.262	8.8RP 4.1/12.4	9RP 3.9/14	Vivid purplish red.
Harvard Crimson	70050	.087	.434	.274	0.7R 3.4/10.3	1.5R 3.2/12	Deep purplish red.
Ruby	70051	.083	.443	.265	8.8RP 3.4/9.2	0.4R 3.1/10.4	Do.
American Beauty	70052	.059	.465	.263	0.2R 2.8/8.8	1R 2.6/11	Do.
Magenta	70053	.056	.455	.261	9.3RP 3.0/9.0	1R 2.8/11	Do.
Redgrape	70054	.049	.426	.251	8.2RP 2.6/7.8	10RP 2.2/9	Very dark purplish red.
Lavender	70055	.300	.300	.271	5.5P 6.0/4.8	5.7P 6.1/4.1	Pale purple.
Lilac	70056	.187	.303	.248	6.5P 4.9/6.4	6.6P 4.9/5.5	Moderate purple.
Mauve	70057	.172	.287	.216	5.2P 4.7/9.3	5.2P 4.6/8.7	Do.
Violet	70058	.130	.259	.184	2.6P 4.2/11.0	2.6P 4.1/9.7	Strong purple.
Pansy	70059	.044	.234	.147	0.9P 2.4/10.0	1P 2.2/10	Deep bluish purple.
Purple	70060	.027	.241	.165	.6P 1.8/6.9	1P 1.6/8	Dark bluish purple.
Spring Green	70061	.348	.353	.459	6.3GY 6.4/7.2	6.8GY 6.2/6.8	Moderate yellowish green.
Mintleaf	70062	.289	.324	.458	8.8GY 5.9/7.6	9.6GY 5.7/7.5	Do.
Emerald	70063	.163	.286	.478	1.2G 4.6/8.2	1.4G 4.5/8.8	Do.
Hunter	70064	.070	.290	.434	1.0G 3.1/5.1	1.5G 2.8/4.6	Very dark yellowish green.
Myrtle	70065	.074	.264	.397	4.5G 3.2/5.1	5.2G 2.9/4.3	Dark green.
Bottle Green	70066	.043	.281	.363	4.9G 2.4/2.9	4.1G 2.1/2.6	Very dusky green.
Jasmine	70067	.659	.414	.424	3.6Y 8.4/7.7	3.5Y 8.2/8.0	Moderate yellow.
Spanish Yellow	70068	.525	.482	.448	0.4Y 7.6/12.2	10YR 7.6/11	Strong yellowish orange.
Orange	70069	.380	.516	.419	5.7YR 6.6/12.7	5YR 6.6/13	Strong orange.
Princeton Orange	70070	.347	.519	.409	4.3YR 6.4/12.5	3.3YR 6.4/12.6	Do.

TABLE 5.—*Adopted color specifications for the TCCA Standard Color Card of America, ninth edition, and the U. S. Army Color Card*—Continued

TCCA name	Cable number	ICI specification			Munsell		ISCC-NBS color designation
		Y	*x*	*y*	Renotation, *H V/C*	Book notation, *H V/C*	
STANDARD COLOR CARD OF AMERICA—Continued							
Golden Poppy	70071	0.264	0.555	0.386	1.6YR 5.7/13.8	1YR 5.6/14	Strong reddish orange.
Indian Orange	70072	.203	.560	.359	9.4R 5.1/13.2	9R 5.1/14	Do.
Periwinkle	70073	.166	.253	.227	8.7PB 4.6/6.8	8.8PB 4.5/6.6	Moderate bluish purple.
Cornflower Blue	70074	.110	.222	.176	8.4PB 3.8/9.8	9PB 3.8/11	Strong bluish purple.
Old Glory Blue	70075	.040	.229	.186	8.2PB 2.3/6.1	8.6PB 2.1/5.3	Dark bluish purple.
Independence	70076	.030	.241	.209	7.8PB 2.0/4.3	8.0PB 1.8/3.1	Dusky bluish purple.
National Flag Blue	70077	.025	.259	.238	7.6PB 1.7/2.5	8PB 1.5/1.8	Dusky purplish blue.
Homage Blue	70078	.023	.269	.252	7.7PB 1.7/2.0	8PB 1.5/1.4	Purplish black.
Geranium	70079	.201	.599	.297	2.7R 5.0/14.0	3R 5.0/15	Vivid purplish red.
Scarlet	70080	.153	.567	.307	4.9R 4.5/14.9	5R 4.4/15	Vivid red.
Cardinal	70081	.086	.528	.300	4.1R 3.4/10.6	4R 3.3/12	Deep red.
Dark Cardinal	70082	.056	.480	.290	2.8R 2.8/7.7	4R 2.5/10	Do.
Garnet	70083	.041	.422	.294	3.0R 2.3/4.9	4.6R 2.0/7.0	Very dark red.
Maroon	70084	.042	.383	.294	1.0R 2.4/3.5	2.9R 2.1/3.9	Very dusky purplish red.
Lustre Blue	70085	.081	.213	.188	6.6PB 3.3/7.9	6.8PB 3.2/8.3	Moderate purplish blue.
Tale Blue	70086	.063	.204	.165	7.3PB 2.9/8.8	7.2PB 2.9/9.1	Strong purplish blue.
Royal Blue	70087	.041	.195	.153	6.9PB 2.3/8.4	7.3PB 2.1/7.7	Dark purplish blue.
Navy 1	70088	.039	.238	.226	5.8PB 2.3/3.9	6.2PB 2.1/2.8	Dusky purplish blue.
Navy 2	70089	.027	.240	.230	5.7PB 1.8/3.2	6.0PB 1.7/2.6	Do.
Midnight	70090	.022	.263	.255	6.0PB 1.6/1.9	6PB 1.4/1.5	Bluish black.
Champagne	70091	.518	.366	.358	8.5YR 7.6/3.5	9.2YR 7.5/4.0	Pale to weak orange.
Cork	70092	.237	.393	.366	6.8YR 5.4/4.0	7.3YR 5.4/4.1	Light brown.
Sandalwood	70093	.178	.392	.362	6.0YR 4.8/3.6	6.9YR 4.6/3.3	Do.
Oakwood	70094	.124	.411	.366	5.2YR 4.1/3.7	5.5YR 3.8/3.3	Moderate brown.
Tobacco	70095	.053	.418	.358	4.3YR 2.7/3.1	4.2YR 2.5/3.7	Dark brown.
African Brown	70096	.046	.347	.331	4.7YR 2.5/1.1	5YR 2.4/1.2	Brownish black.
Vassar Rose	70097	.387	.379	.298	8.1RP 6.7/8.1	9RP 6.5/9	Light purplish red.
Peach Blossom	70098	.242	.422	.291	9.2RP 5.5/10.3	9.5RP 5.2/10.3	Strong purplish red.
Strawberry	70099	.148	.418	.283	8.8RP 4.4/8.8	9.8RP 4.1/8.6	Moderate purplish red.
Raspberry	70100	.090	.425	.273	8.6RP 3.5/8.2	9.5RP 3.3/8.7	Dark purplish red.
Claret	70101	.036	.374	.287	9.9RP 2.2/3.4	1.3R 1.8/3.8	Very dusky purplish red.
Burgundy	70102	.032	.354	.289	8.7RP 2.0/2.3	0.5R 1.6/2.0	Very dusky red purple.
Ecru	70103	.343	.353	.354	0.9Y 6.4/2.3	1.4Y 6.2/2.3	Pale brown.
Beige	70104	.245	.368	.355	7.8YR 5.5/2.8	8.4YR 5.4/3.0	Do.
Fawn	70105	.178	.370	.356	8.1YR 4.8/2.6	8.7YR 4.7/2.5	Do.
Beaver	70106	.127	.366	.351	7.6YR 4.1/2.0	8YR 4.0/1.9	Weak brown.
Autumn Brown	70107	.058	.396	.363	7.1YR 2.8/2.5	8.2YR 2.6/2.7	Do.
Seal	70108	.043	.357	.342	7.1YR 2.4/1.3	9YR 2.1/1.6	Dusky brown.
Old Blue	70109	.345	.293	.304	1.2PB 6.4/1.7	10B 6.2/1.2	Medium bluish gray.
Mistiblu	70110	.192	.286	.293	3.5PB 4.9/2.0	3PB 4.8/1.5	Pale purplish blue.
West Point	70111	.091	.279	.286	3.6PB 3.5/1.7	2PB 3.4/1.4	Dark bluish gray.
Bluesteel	70112	.073	.271	.276	4.0PB 3.2/2.0	3PB 3.1/1.8	Weak purplish blue.
Stone Blue	70113	.069	.275	.271	6.0PB 3.1/2.0	6PB 3.0/1.8	Do.
Graphite Blue	70114	.032	.267	.261	6.2PB 2.0/2.0	6PB 1.9/1.4	Bluish black.
Amberlite	70115	.371	.414	.389	8.6YR 6.6/5.9	8.8YR 6.4/5.7	Dusky yellowish orange.
Topaz	70116	.311	.438	.394	7.3YR 6.1/6.8	7.2YR 5.9/6.8	Weak orange.
Burnished Straw	70117	.209	.430	.380	5.8YR 5.1/5.5	6.1YR 5.2/5.6	Light brown
Gold Brown	70118	.156	.456	.374	3.4YR 4.5/6.2	3.6YR 4.3/6.1	Moderate brown.
Brown	70119	.071	.441	.368	4.2YR 3.1/4.2	4.3YR 2.8/4.3	Do.
Caramel Brown	70120	.047	.431	.354	3.1YR 2.5/3.5	3YR 2.2/4	Dusky reddish brown.

TABLE 5.—*Adopted color specifications for the TCCA Standard Color Card of America, ninth edition, and the U. S. Army Color Card*—Continued

TCCA name	Cable number	ICI specification			Munsell		ISCC-NBS color designation
		Y	x	y	Renotation, *H V/C*	Book notation, *H V/C*	
STANDARD COLOR CARD OF AMERICA—Continued							
Starlight Blue	70121	0.407	0.283	0.288	5.2PB 6.8/3.2	5.6PB 6.6/2.7	Very pale purplish blue.
Lupine	70122	.273	.264	.264	5.6PB 5.8/5.0	6.0PB 5.5/4.7	Pale purplish blue.
Hydrangea Blue	70123	.136	.248	.243	5.7PB 4.2/5.1	6.0PB 4.1/5.2	Moderate purplish blue.
Grecian Rose	70124	.312	.390	.331	6.8R 6.1/5.5	7.1R 5.9/5.1	Weak reddish orange.
Bois de Rose	70125	.190	.419	.331	6.6R 4.9/6.1	7.2R 4.9/5.0	Do.
Mahogany	70126	.057	.421	.325	6.8R 2.8/3.8	8R 2.5/4	Very dusky red.
Sunset	70127	.598	.377	.365	8.2YR 8.0/4.4	8.6YR 8.1/5.2	Weak yellowish orange.
Tan	70128	.334	.389	.374	8.7YR 6.3/4.4	9.0YR 6.1/4.3	Light yellowish brown.
Maple Sugar	70129	.182	.414	.387	9.0YR 4.8/4.5	9.1YR 4.8/4.4	Moderate yellowish brown.
Almond Green	70130	.182	.310	.352	0.2G 4.8/2.0	10GY 4.6/1.7	Weak green.
Blue Spruce	70131	.138	.284	.346	7.3G 4.3/2.8	7.5G 4.0/2.1	Weak blue green.
Jungle Green	70132	.042	.267	.337	1.1BG 2.4/2.7	0.6BG 2.2/2.1	Very dusky green.
Orchid	70133	.418	.311	.275	7.5P 6.9/5.8	8P 6.7/5	Light reddish purple.
Amethyst	70134	.104	.306	.226	7.4P 3.8/7.2	7.0P 3.7/6.2	Moderate purple.
Plum	70135	.041	.298	.222	6.4P 2.3/4.9	6.5P 2.2/4.1	Very dusky purple.
Sand	70136	.404	.336	.341	1.4Y 6.8/1.5	2.6Y 6.8/1.6	Yellowish gray.
Castor	70137	.081	.342	.340	9.8YR 3.3/1.0	1Y 3.1/1.0	Brownish gray.
Taupe	70138	.060	.340	.336	8.6YR 2.9/0.9	10YR 2.8/0.9	Do.
Nude	70139	.346	.352	.347	8.4YR 6.4/2.2	9.3YR 6.3/2.4	Pale brown.
Toast Brown	70140	.135	.401	.355	3.6YR 4.2/3.7	4.2YR 4.0/3.0	Weak to moderate brown.
Spicebrown	70141	.053	.416	.355	3.6YR 2.7/3.1	3.6YR 2.4/3.5	Dark brown.
Brittany Blue	70142	.236	.247	.275	8.6B 5.4/4.8	7.7B 5.2/4.2	Weak blue.
Old China	70143	.128	.230	.246	1.5PB 4.1/5.4	1.0PB 4.0/5.3	Moderate blue.
Peasant Blue	70144	.087	.239	.245	3.4PB 3.4/4.2	3.1PB 3.2/4.0	Dusky blue.
Aqua	70145	.259	.270	.315	8.0BG 5.6/3.0	7.1BG 5.4/3.0	Moderate blue green.
River Blue	70146	.143	.260	.303	1.1B 4.3/3.0	8.2BG 4.2/2.8	Do.
Teal	70147	.067	.232	.271	5.3B 3.0/3.3	5.3B 2.9/3.3	Dusky Blue.
Peach	70148	.554	.395	.358	3.5YR 7.8/5.7	5YR 7.8/7	Pale to light orange.
Crab Apple	70149	.293	.403	.345	7.7R 5.9/11.5	7.4R 5.9/12.2	Strong reddish orange.
Lacquer	70150	.123	.511	.334	7.3R 4.0/9.5	7.5R 3.8/10.2	Dark reddish orange.
Silver	70151	.310	.322	.325	8.0YR 6.1/0.6	10YR 6.1/0.6	Light brownish gray.
Nickel	70152	.286	.314	.316	1.2R 5.9/0.5	10RP 5.9/0.3	Medium gray.
Steel	70153	.171	.309	.307	6.3P 4.7/0.8	7P 4.6/0.5	Medium purplish gray.
Limepeel	70154	.285	.380	.450	2.7GY 5.9/6.0	2.8GY 5.7/5.5	Moderate yellow green.
Moostone	70155	.197	.375	.441	2.7GY 5.0/5.0	3.0GY 4.9/5.0	Dark yellow green.
Olive	70156	.081	.357	.415	3.1GY 3.3/3.2	3.1GY 3.1/4.5	Moderate olive green.
Old Gold	70157	.313	.433	.428	2.3Y 6.1/6.9	2.4Y 5.9/6.2	Dusky yellowish orange.
Gold	70158	.266	.445	.427	1.3Y 5.7/7.1	1.1Y 5.5/7.0	Strong yellowish brown.
Bronze	70159	.088	.414	.402	1.8Y 3.5/3.8	2Y 3.2/4	Dark yellowish brown.
Burnt Orange	70160	.184	.506	.373	1.5YR 4.8/9.2	1.2YR 4.8/9.8	Moderate reddish orange.
Terra Cotta	70161	.088	.494	.350	9.8R 3.5/7.0	9.9R 3.2/8.0	Moderate reddish brown.
Henna	70162	.080	.454	.342	9.4R 3.3/5.3	9.8R 3.0/5.8	Do.
Heliotrope	70163	.110	.343	.256	2.3RP 3.8/5.9	2.5RP 3.6/5.4	Moderate red purple.
Prune	70164	.030	.311	.237	8.6P 2.0/4.0	8.5P 1.8/3.2	Very dusky reddish purple.
Eggplant	70165	.030	.306	.279	7.5P 1.9/1.5	7P 1.8/1.2	Purplish black.

TABLE 5.—*Adopted color specifications for the TCCA Standard Color Card of America, ninth edition, and the U. S. Army Color Card*—Continued

TCCA name	Cable number	ICI specification			Munsell		ISCC-NBS color designation
		Y	*x*	*y*	Renotation, *H V/C*	Book notation, *H V/C*	
STANDARD COLOR CARD OF AMERICA—Continued							
Jade Green	70166	0.267	0.320	0.401	8.8GY 5.7/4.6	8.8GY 5.6/4.1	Weak yellowish green.
Primitive Green	70167	.156	.247	.450	3.6G 4.5/8.9	4.1G 4.4/8.5	Strong green.
Irish Green	70168	.081	.224	.460	4.0G 3.3/8.8	5G 3.1/8	Deep green.
Putty	70169	.305	.332	.330	6.5YR 6.0/1.2	7.5YR 6.0/1.2	Light brownish gray.
Pigeon	70170	.196	.325	.317	4.1R 5.0/1.1	6R 5.0/0.7	Reddish gray.
Smoke	70171	.061	.321	.316	5.1R 2.9/0.4	10R 2.9/0.4	Dark gray.
Purple Orchid	70172	.097	.323	.187	9.3P 3.6/12.1	10P 3.3/11	Deep reddish purple.
Dahlia Purple	70173	.057	.296	.171	7.0P 2.8/10.2	8P 2.6/10	Do.
Imperial Purple	70174	.054	.306	.195	7.9P 2.7/8.0	8.3P 2.6/7.6	Do.
Saxe Blue	70175	.205	.250	.269	0.8PB 5.1/4.6	0.8PB 5.0/4.2	Weak blue.
Electric	70176	.094	.225	.254	8.6B 3.6/4.6	7.8B 3.4/4.2	Dusky blue.
Majolica Blue	70177	.088	.220	.235	1.6PB 3.5/5.3	1.4PB 3.3/5.0	Dusky to dark blue.
Shrimp Pink	70178	.301	.478	.317	4.0R 6.0/12.8	5R 5.9/13	Brilliant red.
Apple Red	70179	.142	.551	.309	4.8R 4.3/13.6	5R 4.2/14	Vivid red.
Old Glory Red	70180	.082	.560	.308	5.5R 3.3/11.1	5R 3.1/14	Do.
Chalk Pink	70181	.497	.362	.323	5.0R 7.4/4.6	6.1R 7.4/4.8	Moderate pink.
Old Rose	70182	.282	.383	.310	1.1R 5.8/6.3	2.2R 5.7/6.5	Light purplish red.
Goldmist	70183	.425	.378	.397	5.3Y 7.0/4.5	6.6Y 7.0/4.6	Weak greenish yellow.
Lt. Olive Drab	70184	.097	.386	.381	1.8Y 3.6/2.7	2.2Y 3.5/2.8	Weak brown.
Gull	70185	.389	.325	.325	5.0YR 6.7/0.9	5YR 6.7/1.0	Pinkish gray.
Grebe	70186	.092	.318	.319	1.8YR 3.5/0.3	10YR 3.5/0.2	Dark gray.
Flax	70187	.399	.369	.369	1.2Y 6.8/3.5	1.7Y 6.8/3.4	Weak yellowish orange.
Khaki	70188	.276	.366	.365	1.1Y 5.8/2.7	1.2Y 5.7/2.9	Pale brown.
Ashes of Rose	70189	.214	.359	.288	5.5RP 5.2/5.9	6.0RP 5.1/5.7	Moderate red purple.
Catawba	70190	.044	.360	.267	5.0RP 2.4/4.7	6.9RP 2.2/3.6	Very dusky red purple.
Rose Beige	70191	.310	.383	.354	4.5YR 6.1/4.0	5.5YR 6.0/4.0	Light brown.
Cocoa	70192	.102	.417	.351	1.9YR 3.7/4.0	2.8YR 3.3/3.7	Moderate brown.
Pearl Gray	70193	.388	.324	.330	2.3Y 6.7/0.7	3Y 6.6/0.9	Yellowish gray.
Dusty Pink	70194	.392	.369	.338	0.4YR 6.7/3.9	1.4YR 6.6/3.6	Moderate orange pink
Dustblu	70195	.252	.285	.292	4.3PB 5.6/2.4	3.6PB 5.4/1.9	Pale purplish blue.
Chamois	70196	.379	.390	.395	1.5Y 6.6/5.1	1.6Y 6.5/4.9	Light yellowish brown.
Crayon Green	70197	.494	.313	.379	10.0GY 7.4/4.2	0.1G 7.2/4.2	Pale yellowish green.
Violine Pink	70198	.206	.378	.267	4.8RP 5.1/9.0	4.7RP 4.8/9.3	Strong red purple.
Natural	70199	.454	.339	.342	0.6Y 7.2/1.7	1Y 7.1/1.9	Very pale brown.
Spraygreen	70200	.379	.306	.342	1.7G 6.6/1.9	1G 6.6/1.6	Pale green.
Bisque	70201	.351	.362	.350	7.0YR 6.4/2.8	7.8YR 6.3/3.2	Light brown.
Crocus	70202	.340	.324	.271	0.2RP 6.3/6.4	0.6RP 6.1/6.7	Light reddish purple.
Popcorn	70203	.508	.412	.416	2.8Y 7.9/7.2	2.7Y 7.9/7.3	Moderate yellow.
Robin's Egg	70204	.222	.273	.301	4.7B 5.3/2.5	1.8B 5.2/2.2	Weak blue.
Lemon Yellow	70205	.603	.424	.443	4.7Y 8.1/8.7	4.4Y 8.2/8.9	Moderate yellow.
Coral	70206	.450	.426	.314	2.5R 7.1/10.6	5R 7.0/12	Vivid pink.
Parrot Blue	70207	.232	.222	.297	10.0BG 5.4/6.5	9.2BG 5.1/6.1	Moderate greenish blue.
Chartreuse	70208	.492	.418	.471	9.2Y 7.4/9.0	9.0Y 7.4/8.3	Moderate greenish yellow.
Oriental Blue	70209	.102	.176	.168	4.5PB 3.7/11.1	5PB 3.4/14	Vivid purplish blue.
Carmine	70210	.126	.533	.286	2.7R 4.1/13.8	3R 3.9/14	Vivid purplish red.
Bluebird	70211	.112	.217	.226	2.9PB 3.9/6.4	2.9PB 3.7/6.7	Moderate blue.
Parma Violet	70212	.131	.254	.187	1.7P 4.2/10.5	1.8P 4.1/9.7	Strong bluish purple
Fuchsia	70213	.129	.404	.195	3.3RP 4.1/17.2	4RP 3.8/16	Vivid red purple.
Scarab Green	70214	.302	.256	.420	4.3G 6.0/9.3	4.2G 6.0/7.7	Brilliant green.
Nugget Gold	70215	.345	.457	.462	3.9Y 6.4/9.3	3Y 6.3/9	Dark to deep yellow.
Sapphire Blue	70216	.049	.202	.145	7.9PB 2.6/10.0	8.3PB 2.4/9.6	Deep bluish purple.

TABLE 5.—*Adopted color specifications for the TCCA Standard Color Card of America, ninth edition, and the U. S. Army Color Card*—Continued

TCCA name	Cable number	ICI specification			Munsell		ISCC-NBS color designation
		Y	x	y	Renotation, *H V/C*	Book notation, *H V/C*	
UNITED STATES ARMY COLOR CARD							
Golden Yellow	65001	0.449	0.474	0.458	2.0Y 7.1/11.3	1Y 7.3/11	Strong yellowish orange.
Yellow	65002	.414	.510	.438	7.8YR 6.9/13.2	7YR 6.5/12	Strong orange.
Golden Orange	65003	.316	.510	.399	3.8YR 6.1/11.4	3.1YR 5.9/11.9	Do.
Orange	65004	.212	.559	.361	9.5R 5.2/13.2	9R 5.2/14	Strong reddish orange.
White	65005	.677	.329	.335	1.8Y 8.5/1.2	3Y 8.8/1.7	Yellowish white.
Scarlet	65006	.102	.548	.320	6.1R 3.7/11.2	6R 3.3/13	Deep to vivid red.
Green	65007	.078	.295	.403	1.2G 3.3/4.2	1.8G 2.9/3.3	Very dark yellowish green.
Silver Gray	65008	.309	.319	.324	1.0Y 6.1/0.5	1Y 6.0/0.4	Medium gray.
Pansy	65009	.058	.247	.166	1.4P 2.8/9.1	2P 2.6/9	Moderate bluish purple.
Ultramarine Blue	65010	.051	.180	.127	7.0PB 2.6/11.8	7.5PB 2.2/11.6	Deep purplish blue.
Cobalt Blue	65011	.045	.231	.205	6.9PB 2.5/5.2	7.2PB 2.3/4.0	Dusky purplish blue.
Dark Blue	65012	.027	.301	.304	7.3PB 1.8/0.4	5PB 1.6/0.3	Black.
Crimson	65013	.083	.485	.276	0.8R 3.4/10.2	2R 3.2/12	Deep purplish red.
Light Blue	65014	.234	.265	.287	9.0B 5.4/3.4	7.3B 5.2/2.9	Weak blue.
Buff	65015	.468	.398	.382	9.0YR 7.2/5.4	9.6YR 7.1/5.4	Weak yellowish orange.
Brown	65016	.072	.415	.363	5.0YR 3.1/3.3	5.0YR 2.8/3.5	Moderate brown.
Maroon	65017	.044	.378	.307	3.3R 2.4/2.7	4.7R 2.1/2.5	Very dusky red.
Black	65018	.027	.305	.309	8.1PB 1.8/0.2	9B 1.7/0.1	Black.
Sky Blue	65019	.041	.238	.230	5.3PB 2.4/3.8	5.8PB 2.1/2.9	Dusky purplish blue.
Brick Red	65020	.063	.508	.326	6.8R 3.0/7.5	7.5R 2.5/10	Deep reddish brown.
Old Gold	65021	.303	.425	.427	3.1Y 6.7/7.1	2.9Y 6.8/6.6	Moderate yellow.
Mosstone	65022	.203	.362	.442	4.8GY 5.0/5.1	4.6GY 4.9/5.6	Dark yellow green.

The adopted values given in table 5 were based upon the measured values given in table 2, A and B. For all nonfluorescent and weakly fluorescent samples that were cross-checked (see table 3), there is no basis for doubting the reliability of the spectrophotometric result. Accordingly, the spectrophotometric values for the chromaticity coordinates, x and y, were adopted. The remaining samples, which were too far in color from the nearest neighbor for cross-checking, were checked by comparison with Munsell standards on the chromaticity-difference colorimeter. For these samples the adopted values are equally weighted means of the spectrophotometric values and those by way of the Munsell standards. Before averaging, however, the results by this alternate method were corrected by the addition of 0.010 to correspond to the greater amount of surface-reflected energy collected by the spectrophotometer; see eq 4 and 4b. For samples classed as strongly fluorescent, however, the spectrophotometer cannot be relied upon. The adopted values are therefore based only on comparisons with the Munsell standards by means of the chromaticity-difference colorimeter adjusted to the amount of surface-reflected energy corresponding to the angular illuminating and viewing conditions of the recording spectrophotometer.

A similar plan was followed in deriving adopted values of daylight reflectance for the samples of the standard card. The spectrophotometric result for all but 21 of the nonfluorescent and weakly fluores-

cent samples was averaged with the multipurpose-reflectometer result corrected by the addition of 0.010. For the 21 nonfluorescent and weakly fluorescent samples measured by means of the Macbeth-Martens reflectometer, the adopted values consist of equally weighted means of three independent determinations each, one by the spectrophotometer, one by the multipurpose reflectometer plus a correction of 0.010, and one by the Macbeth-Martens reflectometer plus a correction of 0.011. For the strongly fluorescent samples of the standard card, however, only the latter determination was given weight, neither the spectrophotometer nor the multipurpose reflectometer being applicable.

A slightly different plan was followed in deriving adopted values of daylight reflectance for the samples of the Army card. The grosgrain weave of these samples is such that in one of the positions used for measurement by the multipurpose and Macbeth-Martens reflectometers (ridges in plane of illuminant) an excess of surface-reflected light is collected, and in the other (ridges perpendicular to plane of illuminant), a deficiency; therefore, no correction was applied to the average.

The Munsell renotations in table 5 were found from the ICI specifications of columns 3, 4, and 5, in accord with the recommendations of the OSA Subcommittee on the Spacing of the Munsell Colors [26]. The renotation values were found from table II of the report of that subcommittee, and the renotation hue and chroma, from large-scale plots of figures 1 to 9 of that report. The Munsell book notations were also found from the ICI specifications of columns 3, 4, and 5. The process of conversion is the reverse of that described in section III, 5. The ISCC–NBS color designations in the last column were found from these book notations in the usual way [18], except that a number of samples that fall on the boundary between two color designations have been given a single rather than a double designation by carrying out the conversion to Munsell book notations to one more decimal place than is given in this table.

It will be noted that the ISCC–NBS designations often correlate well with the TCCA name, and in these cases the two designations supplement each other in a useful way. There are, however, a number of notable exceptions, such as 70078, 70178, 65002, and 65020. A study of these exceptions shows that minor revisions of the ISCC–NBS boundaries are quite feasible that would bring the method into considerably improved agreement with accepted color terminology in textiles. It is possible that a proposal for such boundary revisions will be submitted to the Inter-Society Color Council.

Table 6 gives TCCA cable numbers, visually estimated Munsell book notations, and departures of these book notations from the adopted values of table 5. The uncertainty of these estimated book notations is equivalent to about two-thirds of a hue step, two-tenths of a value step, and one-half of a chroma step, except for those found by extrapolation over a considerable range, in which case the uncertainty of the chroma estimation may easily be double this amount. Notations uncertain because of extrapolation are given only to the nearest hue and chroma step; others, except hues of low-chroma samples, to tenths. The average hue, value, and chroma differences are, respectively, 0.5 (for samples of chroma greater than 2.0), 0.1, and 0.4. From the generally negligible size of these departures, it

may be seen that as intended, the methods of deriving the adopted values are such as to conform to the customary method of using the TCCA standards, that is, comparison of unknown colors with them by light from the sky through a vertical window.

TABLE 6.—*Visually estimated Munsell book notations of the TCCA color standards, and the differences between these estimates and the adopted book notations*

Cable number	Estimated Munsell book notation	Differences (estimated—adopted)			Cable number	Estimated Munsell book notation	Differences (estimated—adopted)		
		Hue	Value	Chroma			Hue	Value	Chroma
STANDARD COLOR CARD OF AMERICA									
70001	2.5Y 9.2/0.3	0.0	+0.1	−0.4	70056	7.0P 4.9/5.0	+1.0	0.0	−0.3
70002	2.5Y 9.2/1.0	+.5	+.1	−.6	70057	5.5P 4.5/8.5	+0.3	−.1	−.2
70003	2.5Y 9.0/1.8	−1.5	−.1	−.4	70058	3.0P 4.0/9.0	+.4	−.1	−.7
70004	2.5Y 8.4/2.8	+0.2	+.1	−.3	70059	2P 2.2/10	+1	.0	0
70005	2.5Y 8.4/4.8	.0	+.1	.0	70060	10PB 1.6/8	−1	.0	0
70006	2.0Y 8.3/7.2	+1.0	+.1	−.2	70061	7.5GY 6.2/7.0	+0.7	.0	+.2
70007	10B 8.2/0.8	+2	.0	+.1	70062	9.8GY 5.9/9.0	+.2	+.2	+1.1
70008	1.5PB 7.5/2.5	+1.9	−.1	+.3	70063	1.5G 4.4/9.0	+.1	−.1	+0.2
70009	10.0B 7.5/3.5	0.0	−.1	+.7	70064	2.0G 2.9/4.8	+.5	+.1	+.2
70010	1.0PB 6.5/3.8	+2.0	+.1	+.8	70065	5.0G 3.0/4.5	−.2	+.1	+.2
70011	2.0PB 6.6/4.0	+0.8	−.1	−.6	70066	3.0G 2.1/2.2	−1.1	.0	−.4
70012	1.0PB 6.3/7.0	+.3	.0	+.1	70067	3.0Y 8.4/8.0	−0.5	+.2	.0
70013	10R 8.5/2	+1	.0	0	70068	10YR 7.6/11	0	.0	0
70014	6R 8.3/5	0	−.2	0	70069	5YR 6.4/12	0	−.2	−1
70015	6R 8.0/6	+1	+.1	0	70070	4.0YR 6.2/12.5	+.7	−.2	−0.1
70016	3R 7.6/7	−1	−.1	0	70071	1YR 5.4/14	0	−.2	0
70017	3.0R 7.0/10.0	+0.8	−.2	−.2	70072	10R 5.0/16	+1	−.1	+1
70018	2.5R 6.3/8.5	.0	+.1	−.9	70073	9.0PB 4.6/6.0	+0.2	+.1	−0.6
70019	8BG 7.9/2.0	+1	+.2	+.7	70074	9PB 3.9/8	0	+.1	−.2
70020	6.5BG 7.2/4.0	−1.0	+.1	−.1	70075	8.5PB 2.0/5.1	−.1	−.1	−0.1
70021	2.0B 6.3/6.0	+0.1	+.1	.0	70076	8.8PB 1.9/3.5	+.8	+.1	+.4
70022	4.5B 5.2/6.0	−.8	.0	−.7	70077	8PB 1.4/1.8	0	−.1	.0
70023	4.0B 3.4/6.2	+.8	−.2	−.4	70078	8PB 1.3/1.6	0	−.2	+.2
70024	2B 2.5/5	−2	+.1	0	70079	3R 5.1/12	0	+.1	−3
70025	8R 7.9/8	−1	.0	−1	70080	5R 4.2/14	0	−.2	−1
70026	10R 7.5/8	0	−.2	−1	70081	4R 3.3/12	0	.0	0
70027	9R 7.5/9	+1	−.1	−1	70082	3R 2.6/10	−1	+.1	0
70028	8R 7.0/10	+1	+.3	0	70083	4.5R 2.0/8.0	−0.1	.0	+1.0
70029	8R 5.6/10	+1	−.1	−1	70084	3.5R 2.0/5.0	+.6	−.1	+1.1
70030	6.5R 4.9/12.0	−0.2	.0	−0.6	70085	7.0PB 3.1/7.5	+.2	−.1	−0.3
70031	5.0GY 7.6/3.6	+1.1	+.1	+.2	70086	7.0PB 2.8/8.0	−.2	−.1	−1.1
70032	10.0GY 6.6/4.0	.0	+.1	+.7	70087	7.7PB 2.2/3.0	+.4	+.1	+0.3
70033	10.0GY 5.2/2.9	−1.2	−.1	.0	70088	6.5PB 2.2/2.8	+.3	+.1	.0
70034	10GY 4.4/1.8	+1	−.2	.0	70089	6.0PB 1.8/2.2	.0	+.1	−.4
70035	10GY 3.4/2.2	−1	+.2	+.5	70090	6PB 1.2/1.2	0	−.2	−.3
70036	10.0GY 2.1/2.2	−1.0	+.1	−.3	70091	9.5YR 7.3/4.0	+.3	−.2	.0
70037	6.0YR 7.1/6.0	−0.4	+.1	−.1	70092	7.5YR 5.2/3.8	+.2	−.2	−.1
70038	2.5YR 7.2/8.5	+.1	.0	−.5	70093	7.5YR 4.7/3.5	+.6	+.1	+.3
70039	9.0R 6.0/10.5	.0	−.2	−.7	70094	5.0YR 3.6/3.6	−.5	−.2	+.3
70040	7.7R 4.9/12.5	+.7	+.1	+.3	70095	5.0YR 2.5/3.2	+.8	.0	−.3
70041	7.5R 4.3/16	0	−.2	+1	70096	6YR 2.1/1.2	+1	−.3	.0
70042	6R 4.0/15	0	.0	0	70097	10RP 6.3/8	+1	−.2	−1
70043	3.0PB 6.0/4.5	+.5	+.1	−.4	70098	10.0RP 5.1/9.0	+0.5	−.1	−1.3
70044	3.5PB 4.2/4.0	−.8	−.1	−.7	70099	10.0RP 4.1/8.0	+.2	.0	−0.5
70045	2.5PB 4.0/4.5	+.5	+.1	−.2	70100	9.5RP 3.1/8.5	.0	−.2	−.1
70046	4.0PB 3.2/4.3	+.4	+.1	−.4	70101	1.5R 1.7/4.8	+0.2	−0.1	+1.0
70047	3.2PB 2.6/5.5	−.9	−.2	−.4	70102	2R 1.6/2.0	+1.5	.0	0.0
70048	5.0PB 2.2/3.8	−.4	−.1	−.2	70103	1.0Y 6.2/2.5	−0.4	.0	+.2
70049	10RP 4.0/14	+1	+.1	0	70104	9.0YR 5.2/2.4	+.6	−.2	−.5
70050	1.0R 3.1/12	−0.5	−.1	0	70105	9.5YR 4.6/2.5	+.8	−.1	.0
70051	0.5R 3.0/11.0	−.1	−.1	+.6	70106	7YR 3.9/2.0	−1	−.1	+.1
70052	1R 2.6/10	0	.0	−1	70107	8.5YR 2.6/2.5	+0.3	.0	−.3
70053	10RP 2.6/10	−1	−.2	−1	70108	10YR 1.8/2.2	+1	−.2	+.8
70054	10RP 2.1/8	0	−.1	−1	70109	2PB 6.0/1.2	+2	−.2	.0
70055	6.5P 6.1/3.5	+.8	.0	−0.6	70110	3PB 4.9/1.4	−1	+.1	−.1

TABLE 6.—*Visually estimated Munsell book notations of the TCCA color standards, and the differences between these estimates and the adopted book notations*—Con.

Cable number	Estimated Munsell book notation	Differences (estimated−adopted)			Cable number	Estimated Munsell book notation	Differences (estimated−adopted)		
		Hue	Value	Chroma			Hue	Value	Chroma
	STANDARD COLOR CARD OF AMERICA—Continued								
70111	4PB 3.4/1.2	+2	0.0	−0.2	70166	10.0GY 5.6/4.5	+1.2	.0	+.4
70112	4PB 2.9/1.2	+1	−.2	−.6	70167	5.0G 4.6/8.0	+0.9	+.2	−.5
70113	6PB 3.1/1.4	0	+.1	−.4	70168	4G 3.4/8	−1	+.3	0.
70114	8PB 1.9/0.8	+2	.0	−.6	70169	5YR 5.9/0.8	−2.5	−.1	−.4
70115	9.0YR 6.2/5.2	+0.2	−.2	−.5	70170	4R 5.0/0.6	−2.0	.0	−.1
70116	7.2YR 5.8/6.0	.0	−.1	−.8	70171	7.5RP 2.8/0.2	−12.5	−.1	−.2
70117	5.2YR 5.1/5.5	−.9	−.1	−.1	70172	10P 3.4/12	0	+.1	+1
70118	4.5YR 4.1/6.5	+.9	−.2	+.4	70173	9P 2.6/11	+1	.0	+1
70119	4.3YR 2.9/3.8	.0	+.1	−.5	70174	9.0P 2.4/7.5	+0.7	−.2	−0.1
70120	4YR 2.2/4	+1	.0	0	70175	0.5PB 5.0/3.5	−.3	.0	−.7
70121	5.8PB 6.6/2.2	+0.2	0.0	−0.5	70176	7.0B 3.2/4.0	−0.8	−0.2	−0.2
70122	6.0PB 5.4/4.0	.0	−.1	−.7	70177	0.5PB 3.3/4.8	−.9	.0	−.2
70123	5.8PB 4.0/5.0	−.2	−.1	−.2	70178	6R 6.0/12	+1	+.1	−1
70124	7.5R 5.8/4.3	+.4	−.1	−.8	70179	5R 4.0/14	0.0	−.2	0
70125	7.5R 4.7/4.2	+.3	−.2	−.8	70180	5R 3.2/14	.0	+.1	0
70126	9R 2.4/4	+1	−.1	0	70181	6.2R 7.2/4.0	+.1	−.2	−.8
70127	8.8YR 7.9/4.4	+0.2	−.2	−.8	70182	2.5R 5.7/5.5	+.3	.0	−1.0
70128	9.0YR 6.0/4.2	.0	−.1	−.1	70183	7.5Y 6.9/4.8	+.9	−.1	+0.2
70129	9.8YR 4.8/4.0	+.7	.0	−.4	70184	3.0Y 3.7/3.2	+.8	+.2	+.4
70130	2G 4.6/1.8	+2	.0	+.1	70185	10R 6.6/0.4	−5	−.1	−.6
70131	5G 4.0/2.0	−2.5	.0	−.1	70186	2Y 3.5/0.4	+2	.0	+.2
70132	9G 2.0/1.6	−1.6	−.2	−.5	70187	2.0Y 6.9/3.2	+0.3	+.1	−.2
70133	8P 6.6/6	0	−.1	+1	70188	2.0Y 5.6/2.8	+.8	−.1	−.1
70134	7.0P 3.6/5.5	.0	−.1	−0.7	70189	7.0RP 5.0/5.5	+1.0	−.1	−.2
70135	7.0P 2.0/4.2	+.5	−.2	−.1	70190	8.5RP 2.1/3.5	+1.6	−.1	−.1
70136	3Y 7.0/1.2	0	+.2	−.3	70191	6.0YR 5.9/4.5	+0.5	−.1	+.5
70137	10YR 3.1/0.8	−1.0	.0	−.2	70192	2.2YR 3.3/3.8	−.6	.0	+.1
70138	10YR 2.6/0.6	0	−.2	−.3	70193	4Y 6.6/1.0	+1	.0	+.1
70139	9.8YR 6.4/2.0	+.5	+.1	−.4	70194	2.0YR 6.8/3.5	+0.6	+.2	−.1
70140	4.0YR 3.9/3.2	−.2	−.1	+.2	70195	2.0PB 5.4/2.2	−1.6	.0	+.3
70141	4.5YR 2.5/3.2	+.9	+.1	−.3	70196	2.0Y 6.3/4.5	+0.4	−.2	−.4
70142	7.0B 5.2/3.2	−.7	.0	−1.0	70197	10.0GY 7.4/4.2	−.1	+.2	.0
70143	1.5PB 4.1/4.5	+.5	+.1	−0.8	70198	5.5RP 4.8/9.0	+.8	.0	−.3
70144	2.5PB 3.2/4.0	−.6	.0	.0	70199	2Y 7.0/1.4	+1	−.1	−.5
70145	7.0BG 5.5/2.5	−.1	+.1	−.5	70200	2G 6.7/2.2	+1	+.1	+.6
70146	8.0BG 4.0/2.5	−.2	−.2	−.3	70201	7.5YR 6.6/3.2	−0.3	+.3	.0
70147	5.0B 2.8/3.0	−.3	−.1	−.3	70202	2.0RP 6.0/5.8	+1.4	−.1	−.9
70148	4YR 7.6/6	−1	−.2	−1	70203	2.6Y 7.9/8.0	−0.1	.0	+.7
70149	8.0R 5.9/11.5	+0.6	.0	−0.7	70204	1.0B 5.3/2.8	−.8	+.1	−.6
70150	7.0R 4.0/9.2	−.5	+.2	−1.0	70205	5.0Y 8.4/9.5	+.6	+.2	+.6
70151	2Y 5.9/0.4	+2	−.2	−0.2	70206	6R 6.8/11	+1	−.2	−1
70152	10P 5.8/0.3	−10	−.1	.0	70207	9.0BG 5.1/6.0	−0.2	.0	−0.1
70153	5P 4.6/0.3	−2	.0	−.2	70208	10.0Y 7.2/8.2	+1.0	−.2	−.1
70154	3.0GY 5.6/6.0	+0.2	−.1	+.5	70209	4PB 3.5/13	−1	+.1	−1
70155	3.5GY 4.9/5.5	+.5	.0	+.5	70210	2R 4.0/14	−1	+.1	0
70156	3.5GY 3.2/4.5	+.4	+.1	.0	70211	3.0PB 3.6/6.5	+0.1	−.1	−.2
70157	2.5Y 6.0/5.8	+.1	+.1	−.4	70212	2.0P 4.0/8.0	+0.2	−.1	−1.7
70158	2.0Y 5.6/6.0	+.9	+.1	−1.0	70213	4RP 3.9/15	0	+.1	−1
70159	2Y 3.2/4	.0	.0	0	70214	4.7G 5.9/7.2	+.5	−.1	−0.5
70160	1.0YR 4.7/9.2	−.2	−.1	−0.6	70215	4Y 6.2/9	+1	−.1	0
70161	10.0R 3.2/8.0	+.1	.0	.0	70216	8.0PB 2.2/9.5	−0.3	−.2	−.1
70162	10.0R 3.1/6.5	+.2	+.1	+.7					
70163	2.0RP 3.7/4.8	−.5	+.1	−.6					
70164	8.5P 1.7/2.2	.0	−.1	−1.0					
70165	7.5P 1.6/0.8	+.5	−.2	−0.4					

TABLE 6.—*Visually estimated Munsell book notations of the TCCA color standards, and the differences between these estimates and the adopted book notations*—Con.

Cable number	Estimated Munsell book notation	Differences (estimated—adopted)			Cable number	Estimated Munsell book notation	Differences (estimated—adopted)		
		Hue	Value	Chroma			Hue	Value	Chroma
	UNITED STATES ARMY COLOR CARD								
65001	2Y 7.2/10	+1	−0.1	−1	65011	7.0PB 2.1/3.5	−0.2	−0.2	−0.5
65002	7.5YR 6.6/11	+0.5	+.1	−1	65012	6PB 1.8/0.1	+1	+.2	−.2
65003	3.5YR 5.9/11.5	+0.4	.0	−0.5	65013	2R 3.2/11	0	.0	−1
65004	9R 5.0/13	0	−.2	−1	65014	8.0B 5.0/2.2	+.7	−.2	−0.7
65005	4Y 8.7/1.5	+1	−.1	−0.2	65015	10.0YR 7.0/5.0	+.4	−.1	−.4
65006	6R 3.3/12	0	.0	−1	65016	5.0YR 3.0/3.5	.0	+.2	.8
65007	2.0G 3.0/3.2	+.2	−.1	−0.1	65017	5.5R 2.1/3.5	+.8	.0	+1.0
65008	3Y 5.9/0.4	+2	−.1	.0	65018	N 1.8/	-------	+.1	−0.1
65009	2P 2.6/8	0	.0	−1	65019	5.5PB 2.0/3.5	−0.3	−.1	+.6
65010	7.0PB 2.2/10.0	−.5	.0	−1.6	65020	7.5R 2.8/10	0	+.3	0
					65021	2.5Y 6.8/7.0	−.4	.0	+.4
					65022	5.0GY 5.0/6.5	+.4	+.1	+.8

The sources of error discussed in the previous section may combine to yield a rather large possible discrepancy between the adopted book notation and the corresponding visual estimate in table 6. A review of the hue and value differences recorded there, however, indicates that these possibilities have not been realized. There are only five samples (70028, 70096, 70168, 70201, 65020) yielding a value discrepancy as large as 0.3, and the discrepancies in hue greater than one step are ascribable to uncertainties arising from low chroma, extrapolation, or local irregularities in the spacing of the Munsell standards. It may be of interest, however, to review the sources of error that have caused the two outstanding discrepancies in chroma, 3 steps each for Cornflower Blue (70074) and Geranium (70079).

Both of these samples are strongly fluorescent, and the adopted chromas are therefore based entirely upon a comparison with Munsell standards by means of the chromaticity-difference colorimeter. As was often done for samples yielding poor agreement, these comparisons were repeated several times by two observers (GBR, DBJ) and for different Munsell standards with closely agreeing results. From the degree of agreement obtained the uncertainty of the chroma is estimated at 0.4 for Cornflower Blue and 0.3 for Geranium. Cornflower Blue formed a noticeably metameric combination with the neighboring Munsell standards and may have yielded poorer agreement on that account. A correction (eq 4) was then applied for the greater amount of surface-reflected light characteristic of observation before a window. This correction is applied because of the average disparity in angular conditions between the standardized conditions of measurement and the somewhat uncontrolled conditions of use of the samples. From the tristimulus specifications so found (Y, x, y) the Munsell book notations were read by extrapolation with an uncertainty of about 0.5 chroma step for Cornflower Blue and 1.5 for Geranium.

For any one controlled set of angular conditions the visual estimates of chroma for these samples are uncertain by about 1.0 chroma step, the estimate for Geranium because it is obtained by extrapolation,

that for Cornflower Blue by more than the usual 0.5 chroma step because of a local irregularity in the spacing of the Munsell standards. This local irregularity consists of two factors: first, the hue interval from 7.5PB 4/10 to 10PB 4/10 is unusually large making interpolation difficult, and second, the two samples 10PB 4/8 and 10PB 4/10 are nearly alike, making the uncertainty seem more important in terms of book-notation chroma than it really is. The uncertainty introduced by using simple observation before a window rather than controlled angular and spectral distributions is estimated at 0.7 chroma step for both samples. And, finally, Cornflower Blue is one of the few TCCA colors giving significant evidence of impermanence (see table 4). Recent measurements of the unmounted sample indicates that it has decreased in chroma by about 1.0 since the original measurement. The estimate of maximum discrepancy for Cornflower Blue is therefore $0.4+0.5+1.0+0.7+1.0=3.6$ chroma steps, and that for Geranium is $0.3+1.5+1.0+0.7=3.5$. That the observed discrepancies, three steps each, for these colors come so close to the estimate of maximum possible discrepancy is an indication that nearly the maximum of the possible component errors has been realized in each case, and furthermore that the directions of the component errors have agreed so that the effects are cumulative.

This analysis of possible discrepancy serves also to bring out the fact that a large part of it for these two samples (1.5 out of 3.6 for Cornflower Blue, 2.5 out of 3.5 for Geranium) arises from the limitations of the Munsell standards, themselves, their limited range and local irregularities. Samples that can be given a Munsell book notation by interpolation would, of course, generally yield a considerably smaller estimate of maximum possible discrepancy. Furthermore, for the purpose of controlling the color of redyeings of the TCCA standards, the ICI specification, (Y, x, and y) could be used and would have an uncertainty corresponding only to the first component (0.4 chroma step for Cornflower Blue, 0.3 for Geranium).

In conclusion, it may be stated that this measurement in fundamental terms (Y, x, and y) of a set of material color standards widely used in commerce may well mark the beginning of an important new era in the utilization of dyestuffs. Just as the modern automobile with interchangeable parts is made possible by fundamental standards of length combined with accurate and practical secondary length standards, so also may we expect American industry to find important, and as yet largely unforeseen, ways to make use of these sets of secondary standards of color. Only through their relation to a fundamental standard of length do micrometer calipers and gage blocks reach their full usefulness, and likewise the textile color cards require a fundamental colorimetric calibration in order to acquire permanent meaning. The immediate gain to government agencies in simplifying their statements of color requirements through correlation between the Standard Color Card of America and the American War Standard ASA–Z44–1942 can be fairly well assessed now, but the full worth of this work to the textile industry and the consumer will not become known for many years. By sponsoring and supporting this necessary forward-looking step, the Textile Color Card Association has performed a service not only to the textile industry but to all color technology.

VII. SUMMARY

The colors of the samples of the Standard Color Card of America and those of the U. S. Army Color Card have been measured either by means of the recording spectrophotometer or, for fluorescent samples, by colorimetric comparison with standards previously so measured. The resulting color specifications serve as a record against which future dyeings of textile standards may be checked whenever it is desired to know whether they conform under the conditions of use to those measured. These color specifications are given in the three different ways recommended by American War Standard Z44–1942; they are therefore in a form convenient for correlation with existing color specifications so that extension of the already wide use of the TCCA color standards will be facilitated.

It has been shown that although the spectrophotometric technic recommended by Z44–1942 is often inapplicable to fluorescent samples, themselves, colorimetric comparison with nonfluorescent standards previously calibrated by that technic is a practical way of following the provision in Z44–1942 which states that the "spectrophotometer shall be recognized as the basic instrument in the fundamental standardization of color."

The uncertainty ascribable to the various known sources of error (metamerism, variation in angular conditions, variation from sample to sample, errors of interpolation and extrapolation along the Munsell color scales) has been evaluated. It has been shown that the angular condition of the recording spectrophotometer (approximately normal-diffuse) accords somewhat better for these textile samples with the customary condition of viewing before a window than those (45°-normal) recommended by the International Commission on Illumination [30]. And, finally, the reliability of the adopted values has been established by detailed cross-checks and by a comprehensive closing check under the conditions of use. The TCCA standards comprise the first extensive series of material color standards to receive a calibration that has been thus cross-checked in detail. Furthermore, they cover important color ranges not adequately covered by any other set of material color standards calibrated for ICI standard illuminant *C* (average daylight).

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WEARING QUALITY OF EXPERIMENTAL CURRENCY-TYPE PAPERS

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ABSTRACT

Fourteen groups of high-grade papers, differing in fiber composition, were made in the Bureau's experimental paper mill. Papers within the groups differed in the beating treatment of the pulp, in the surface-sizing treatment, and in the use or omission of melamine resin. Of the several kinds of fibers studied, caroa mixed with cotton appears to approach most nearly the desirable characteristics associated with linen-content currency paper. The high-quality wood fibers available do not appear suitable for use in currency paper. Melamine resin in currency-type paper improves folding endurance, tensile and bursting strength, strength after crumpling, stretch, resistance to abrasion, and closure of the sheet. It greatly increases the strength of the paper when wet. However, it makes the dry paper somewhat easier to tear.

CONTENTS

	Page
I. Introduction	249
II. Paper-making equipment	250
III. Paper-making raw materials	250
IV. Making the experimental papers	251
1. Preparation of the rag half-stuff	251
2. Preparation of caroa and sisal pulps	251
3. Beater and paper-machine operations	252
4. Papers containing melamine resin	254
5. Surface sizing the papers	255
V. Methods of testing the papers	256
1. Official methods	256
2. Wear by crumpling	256
3. Surface wear	257
4. Scuffing of wet paper	258
VI. Results of tests	259

I. INTRODUCTION

United States paper currency prior to 1941 was printed on paper composed largely of fibers derived from new linen cuttings imported from Europe. Several hundred tons of linen cuttings were required annually in the manufacture of the currency paper. It became necessary to find suitable substitutes for linen pulp in case of interruption of the foreign supply of linen cuttings. The supply problem was attacked in various ways, being eased by the use of additional cotton

[1] Nearly all members of the Bureau's Paper Section contributed in some measure to this project. It is desired especially to acknowledge the assistance of Martin J. O'Leary and Joshua Missimer in the manufacture of the experimental papers; of Vernon Worthington in the development of the special testing apparatus; and of W. K. Wilson, Thelma L. O'Brian, V. Worthington, Irma G. Callomon, and Alice J. Adams in making the many hundreds of physical and chemical tests of the papers.

fiber to replace a part of the linen and by the use of flax paper-making fiber produced from domestic flax straw. During this time the National Bureau of Standards was engaged on another approach to the problem.

For several years the Bureau has cooperated with the United States Treasury Department in efforts to improve the quality of currency paper and to prolong its useful life. During the period of concern over the supply of linen fiber, this cooperative work has included the use of the Bureau's experimental paper-making and testing equipment to study the paper-making properties of other kinds of fibers that might be available for use in making currency paper, and to evaluate the wearing quality and other pertinent properties of high-grade papers made from these fibers. The work included also some further observations on the effect of variations in paper-making technic, particularly on the effect of melamine resin in currency-type paper.

The papers studied were made in the Bureau experimental paper mill for the threefold purpose of having papers of known composition and history, of having definite information about the paper-making processes used, and of obtaining some unusual combinations of paper-making materials.

Since the previous work at the Bureau on the production of currency paper,[2] some new testing methods have been developed to aid in predicting the serviceability of paper currency, and other testing methods have been improved or standardized. These added tools help to give a better estimate in the laboratory of the properties and behavior of currency-type papers. In addition to the Schopper folding-endurance tester, which has been relied on chiefly in previous work to evaluate the wearing quality of currency paper, the MIT (Massachusetts Institute of Technology) folding-endurance tester, a crumpling apparatus, an air permeameter, and two types of abrasion testers have been used in the present work to aid in evaluating wearing quality.

II. PAPER-MAKING EQUIPMENT

The Bureau's paper mill is equipped to make paper on a semi-commercial scale under practical mill conditions. The equipment employed in the manufacture of the currency papers included a rag cutter; duster; rotary boiler; 50-pound copper-lined wood-tub beater, having manganese-bronze bars and plate, and equipped with a washing cylinder; jordan refiner, with bars of a bronze and steel alloy; four-plate screen; 29-inch Fourdrinier paper-making machine, with wire 33 feet long and having two presses, nine 15-inch dryers, a small machine stack of seven rolls, and a reel; surface-sizing bath and drying cabinet; and a five-roll supercalender.[3]

III. PAPER-MAKING RAW MATERIALS

The fibrous materials employed were the kinds commonly used in currency paper and in other high-grade papers, and in addition two kinds (caroa and sisal) not ordinarily used in this country for the purpose. The linen fiber was obtained from linen cuttings, and the

[2] Tech. Pap. BS 21, 89 (1926) T329; BS J. Research 3, 899 (1929) RP121.

[3] Descriptions and photographs of the equipment are contained in the following publications: Tech. Paper. BS 21, 338-341 (1927) T340; BS J. Research 3, 904-905 (1929) RP121; Paper Trade J. 89, TS194 (Nov. 7, 1929).

cotton fiber, from hosiery clippings and muslin cuttings, all of which, in paper-making parlance, are designated as "new rags." There were four groups of the new rags: light-colored linen cuttings (graded as white and cream); dark-colored linen cuttings (graded as gray and brown); unbleached cotton hosiery clippings; and unbleached muslin. There were also four types of bleached wood pulps—sulfate, sulfite, hard alpha, and soft alpha.[4] In addition, there were two pulps made from leaf fibers, caroa and sisal.

IV. MAKING THE EXPERIMENTAL PAPERS

1. PREPARATION OF THE RAG HALF-STUFF

The procedure followed in the preparation of the rag half-stuff (partially pulped rags that have been boiled, washed, beaten out of weave, and bleached) was essentially the same as the general practice in the commercial production of high-grade papers from rags. It has been described in previous Bureau publications.[5]

The constant factors in the cooking of the rags were as follows:

Weight of oven-dry fiber	106 lb.
Volume of water	52.5 gal.
Initial temperature	70° to 80° F.
Duration of initial temperature	1 hr.
Time for raising to cooking temperature	1 hr.
Cooking temperature	250° to 260° F.
Duration of cooking temperature	5 hr.
Cooking pressure	30 to 40 lb./in.^{2}

Commercial caustic soda (96 percent sodium hydroxide) was used in the cooking liquor to cleanse the rags. The amount used was varied according to the kind of rags being treated. For cotton rags (hosiery and muslin) the amount was 2 percent of the weight of rags; for light-colored linens, 3.5 percent; and for dark-colored linens, 5 percent.

The bleaching operation was begun in the washer (beater used as washer) and was completed in the drainer. Only a small amount of bleaching agent was used to brighten the half-stuff, no attempt being made to bleach it white.

The four groups of rags mentioned in the previous section were kept separate throughout these preparatory processes, until they were blended in the beater.

2. PREPARATION OF CAROA AND SISAL PULPS

Previous work [6] at the Bureau on caroa fiber has shown that the preliminary process employed in the separation of the fiber from the plant is an important factor in determining the properties of the pulp. Description of the procedure used to produce the caroa and sisal pulps from the harvested plant was not supplied, but it is assumed that the plant fibers were cooked, washed, partially bleached, and washed again. For use in currency-type paper it was desirable that the pulps be somewhat whiter than those received. Therefore, they were given additional bleaching and washed again.

[4] Sulfate pulp is a typical strong pulp made by cooking wood by the sulfate process, in which the loss of alkali is made up by adding sodium sulfate. Sulfite is made by cooking chips in an acidic solution, usually bisulfite of calcium. Hard alpha is a sulfate pulp that is given a further purification treatment. Soft alpha is a special form of sulfite wood pulp, highly purified by removing the undesirable forms of cellulose normally found in wood pulps.

[5] Tech. Pap. BS 21, 91 (1926) T329; BS J. Research 3, 902 (1929) RP121; J. Research NBS 14, 651 (1935) RP794.

[6] Tech. Pap. BS 21, 323 (1927) T340.

The sisal pulp as received seemed somewhat raw and therefore was given further cooking before the additional bleaching and washing. The cooking procedure was that usually used at the Bureau for rags. The amounts of chemicals used were 5 percent of lime and 5 percent of sodium sulfite, based on the weight of the dry pulp.

3. BEATER AND PAPER-MACHINE OPERATIONS

The method of beating the half-stuff to prepare it for forming a sheet on the paper machine followed very closely that used for previous experimental production of currency paper and described in a previous publication.[7] The characteristic feature of the method was the gradual lowering of the beater roll.

Before the furnish, that is, the various paper-making materials blended in the beater, was added to the beater, the roll was raised off the plate in order to give clearance to the lumps of half-stuff. The tub was partially filled with water, half-stuff from the drainers was introduced, and additional water was run in until the desired dilution was obtained. After some circulation of the furnish, the roll was gradually lowered, by definite amounts and at fixed intervals, to brush out the fibers and reduce them to optimum length. The position of the beater roll is expressed as the number of turns above (+) or below (−) zero setting, which is the point of contact between the roll and the bedplate. (At settings below zero, the roll is practically freely suspended and riding on the fiber furnish.) Table 1 gives these positions and the corresponding time intervals for the two beating procedures (*A* and *B*) used.

TABLE 1.—*Schedule of roll settings for beating stock*

Procedure *A*		Procedure *B*	
Beating interval	Position of roll [a]	Beating interval	Position of roll [a]
hr		hr	
0	[b] +10	0	[b] +10
¼	[c] +10	¼	[c] +10
¾	+6	¾	+3
1	+5	1	+2
1½	+4	1½	+1
2	+3	2	+½
2½	+2	2½	0
3	+2	3	0
3½	+1½	3½	−½
4	+1½	4	−½
4½	+1	4½	−1
5	+1	5	−1
5½	+½	5½	−1
6	+½	6	−1
6½	+½	6½	−1
7	+½	7	−1
7½	0	7½	−1
8	0	8	−1
8½	0	8½	−1
9	0	9	−1
9½	0		
10	−½		
10½	−½		
11	−½		
11½	−½		
12	−½		

[a] Expressed in turns of the handwheel, which raises or lowers the beater roll. When under positive control, 1 turn of the handwheel changes roll position 0.008 inch.
[b] Quick-raising lever up.
[c] Quick-raising lever down.

[7] Tech. Pap. BS **21**, 96 (1926) T329.

The beaten pulp (stuff, stock) [8] was run into the stuff chest, and from there it was pumped in a continuous stream through the stuff box and the jordan refiner to the paper machine. Pumping the stock from the jordan directly to the paper machine is considered better practice than discharging it into a machine chest and subsequently withdrawing it as needed. By the former (direct) method, changes in the character of the stock indicated as desirable by conditions at the screen, on the paper machine, or in the finished sheet can be effected rapidly by suitable adjustments of the jordan.

The stuff box was of the familiar regulating-box type having a constant head over an adjustable orifice.

Screen plates with 0.024-inch slots were used.

The paper-machine head box (or flow box) was equipped with baffles to mix the stock thoroughly and uniformly as it went to the wire (bronze-wire cloth). There were two slices [9] on the paper machine

The temperature of the stock at the head box was maintained at $110° \pm 2°$ F.

The manipulation of the beater roll (procedure *A* or *B*) and the time of beating the various furnishes are given in table 2. Departures from the beating schedules of table 1 are discussed below. With three exceptions, 48 pounds of pulp was furnished to the beater for each run.

In the preparation of stock for making paper 11 (cotton and hard alpha),[10] beating procedure *A* was followed, except that the beating was continued for an extra hour. It was expected that when rag half-stuff and wood pulp were mixed the circulation would be faster, so the weight of the pulp was increased to 50 pounds. However, the circulation did not increase, necessitating the extra hour of beating. Even then the beaten fiber was considered fairly long, but the stock gave no trouble on the paper machine. Fifty pounds of pulp was also used in preparing stock for making papers 13 and 13M3 (sulfite). Beating procedure *B* was followed to the roll setting of $-\frac{1}{8}$ (see table 1), and the roll was not lowered below this setting. The beating time was 7 hours.

Beating procedure *B* was used in preparing stock for papers 14 and 14M3 (soft alpha), except that the beating was stopped at the end of 8 hours, as the stock was then considered satisfactory. Beating procedure *B* was also used in preparing stock for paper 14x, but the beating time was lengthened to 12 hours.

The caroa and sisal pulps were evidently not refined as much as would be considered desirable for use in currency-type paper, and therefore gave some trouble. The results obtained are not necessarily representative of what might be accomplished under optimum conditions.

The first run of caroa pulp (paper 6x) was beaten for 7 hours by procedure *B*. The stock in the beater felt slimy, doubtless because of the large amount of pithy material in the caroa pulp. The beating shortened the fibers very little, presumably because the pithy material lubricated the surfaces of the beater bars and reduced the cutting and

[8] "Stock" is used in this paper to mean the beaten and refined pulp, together with any added materials, diluted and ready to be formed into paper on the paper machine. It is synonymous with "stuff," but is now more generally used in the paper industry.

[9] The slice is an adjustable crosspiece that controls the depth of the stream of stock that flows on to the paper-machine wire and keeps the surface even. A machine making fine papers usually has two slices.

[10] The grouping of the papers and the designations are explained in note 1 under table 2.

brushing action. An attempt to jordan and screen the stock in the usual way as it flowed to the paper machine was unsuccessful. The fibers collected in bunches in the jordan, which ultimately was used only as a pump. The stock, furthermore, would not go through the 0.024-inch slots in the screen plates. Consequently, it was run through the jordan with the plug pulled away from the bars, and was not screened.

After the pulp for the second run of caroa fiber (paper 6) had been furnished to the beater and circulated for a few minutes, the stock was made acid by the addition of alum (1.9 percent, based on the weight of the dry pulp). Although beaten for 9 hours, the fibers were long. When the stock was being jordanned, at +2 setting, the load on the jordan motor was practically at its capacity. The stock did not screen easily, and continuous scraping of the screen plates was required to keep the stock passing through. The pH at the head box was 5.0. The formation of the finished sheet was "wild" (irregular).

The cotton-caroa stock for paper 7 was made acid with alum (1.5 percent, based on the weight of the dry stock). The pH at the head box was 5.0.

During the beating of the sisal pulp for paper 8, the beater water began to get cloudy shortly after the pulp was added to the beater, as though the pithy, or natural resinous, material was being beaten into a fine suspension. Alum solution was added and the water became clear. The amount of alum used was 2.0 percent of the weight of the dry stock. The beating time (procedure *B*) was reduced to 7 hours. The pH of the stock at the head box was 6.4. The finished paper was well sized and had a very smooth and waxy finish, although neither resin size nor wax had been added.

The cotton-sisal stock for paper 9 was beaten only 8 hours (procedure *B*). It was made acid with alum (1.5 percent of the weight of the dry pulp). The pH at the head box was 6.0. The finished paper was sized somewhat, but not as well as that made from sisal only (paper 8).

4. PAPERS CONTAINING MELAMINE RESIN

The chief reason for retiring paper currency from service is the surface disintegration resulting from wear, which impairs the legibility of the printed matter. Improved bonding between fibers has been achieved very successfully in certain types of paper by the addition of melamine resin during fabrication. To see if it would improve the surface, reducing fuzzing, and lessen the tendency to scuff, crack, and wear away, a small amount of melamine resin (3 percent of the weight of the dry stock) was incorporated in a few of the experimental currency-type papers. Otherwise, each of these papers was made in the same manner as the corresponding unsized paper having the same group number.

For the first trial, paper 10M1 (companion to 10), the prepared melamine-resin solution was added in the machine chest, and the stock was run at pH 6.9, which was obtained by buffering with soda ash (method 1 of adding melamine resin).

For the second trial, paper 10M2, the melamine-resin solution was added continuously to the stock after it left the screen but before it

reached the head box. This method of introduction permitted sufficient agitation and mixing of the melamine-resin solution with the stock at the point of addition. The pH of the stock at the head box was approximately 6.5, with no buffering material added (method 2).

In a third run, paper 10M3, the stock was made slightly acid with alum in the stuff chest, and the melamine-resin solution was added continuously between the screen and the head box (method 3). The pH of the stock leaving the chest, and in the stuff box, before the melamine-resin solution was added, was 5.0, and at the head box it was 4.4. The paper-machine wire was brightened very noticeably, as much as or more than when it is given a regular acid-cleansing treatment.

These three trial runs of hard-alpha pulp indicated that the addition of melamine resin in the chest (method 1) did not develop as much strength in the paper as did methods 2 and 3. Accelerated curing at 260° F for 10 minutes indicated also that the polymerization, or curing, of the resin developed more slowly when method 1 was used than when method 2 or method 3 was used. There was some evidence, however, that excessive use of alum in method 3 to catalyze or hasten the polymerization of the resin may have impaired the permanence of the papers so made.

In making papers 3M2 (companion to 3) and 5M2 (companion to 5), the melamine-resin solution was added according to method 2. The pH at the head box was 6.9 and 6.6, respectively.

In making papers 13M3 (companion to 13) and 14M3 (companion to 14), the melamine-resin solution was added according to method 3, except that the stock was not made quite so acid in the chest. In making paper 13M3, the pH of the stock leaving the chest was 6.6, and of that at the head box, 5.0 to 5.4. In making paper 14M3, the corresponding values were 6.0 to 6.5 and 5.2 to 5.5.

5. SURFACE SIZING THE PAPERS

To facilitate printing the paper by the wet-intaglio process used in making paper currency and to improve the folding endurance and resistance to wear, currency paper is given a surface-sizing treatment with glue. Portions of the 14 groups of experimental papers were similarly surface sized. The waterleaf (unsized) paper was run through a solution of animal glue at approximately 130° F, then between a pair of squeeze rolls to remove the excess sizing solution, and dried in a festoon drier. The desired finish was imparted to the paper by supercalendering.

In these surface-sizing experiments two glue-sizing solutions were used. One contained 4 percent of glue and 0.15 percent of alum (3.75 percent of the weight of the glue), and had a pH of 4.7. The other contained 4 percent of glue and 0.01 percent of formaldehyde (0.25 percent of the weight of the glue), and had a pH of 6.1. The addition of alum or formaldehyde to glue has a tanning effect on the glue, increasing its water resistance and making it more effective as a surface-sizing agent.

Portions of all the papers made, except 6x, were surface sized with the glue-and-alum solution, and other portions of seven of them

were surface sized with the glue-and-formaldehyde solution. (See table 2 and note 1 thereunder.)

V. METHODS OF TESTING THE PAPERS

1. OFFICIAL METHODS

All the physical and chemical tests of the papers were made by the official methods of the Technical Association of the Pulp and Paper Industry,[11] except the tests involving abrasion, crumpling, and the measurement of air permeability. All the physical tests were made under the standard hygrometric conditions of 50-percent relative humidity and 73° F, unless otherwise stated.

2. WEAR BY CRUMPLING

This method of testing has been described in a previous publication,[12] but the crumpling apparatus used in this work differs from that previously described. It is a much simpler, hand-operated apparatus (fig. 1), which crumples the paper under a fixed pressure instead of to a fixed volume. The crumpling cycle is identical with that previously described, although it is not achieved in the same manner.

The photograph (fig. 1) shows the crumpling device and also the device for rolling the specimen (a 2⅝-inch square of paper). The apparatus with which the specimen is rolled consists of a split sheath, *R*, within which there is a two-tined fork integral with a rod that passes through a bearing and terminates in the knob *N*. The specimen of paper is inserted as shown through the slot in the sheath and between the tines of the fork, and is then rolled into a cylinder by rotating knob *N* (which rotates the fork inside the sheath). The entire rolling device is then lifted from its support, and the rolled paper is delivered into the tube *C* by placing the rolling device vertically above the tube, with the open end of the split sheath in contact with the open end of the tube, and then pressing knob *N* downward. This operation pushes the fork, with its engaged roll of paper, into tube *C*, after which the fork is withdrawn and disengaged, leaving the specimen in the tube.

Tube *C* is free to move up and down within the supporting cylindrical guide *B*. Within tube *C* there is a rod or piston (not shown), the lower end of which rests upon the short end of the lever *L*. At the other end of this lever, a weight, *W*, is fastened.

The specimen is crumpled in the following manner. The open end of tube *C* (containing the rolled cylinder of paper) is closed by a cap, *K*, which is locked in place. Tube *C* is then forced downward by hand, the force being communicated from cap *K*, through the roll of paper, to the piston within tube *C* and thence to lever *L*. The limit on the applied pressure is set by the moment of weight *W* which is lifted when the pressure reaches about 150 pounds per square inch.[13] In this process the paper specimen is reduced from a cylinder, 2⅝ inches long, to a crumpled wad, about ½ inch long. Tube *C* is then

[11] Copies of the official methods may be obtained from the Association at 122 East 42d Street, New York 17, N. Y.

[12] J. Research NBS 26, 467 (June 1941) RP1390.

[13] This maximum crumpling pressure was fixed by placing a weight of 22.1 pounds on the piston, which is 11 mm in diameter, and adjusting the position of weight *W* on lever *L* until the two moments were balanced. The weight was then fastened to the lever with a setscrew.

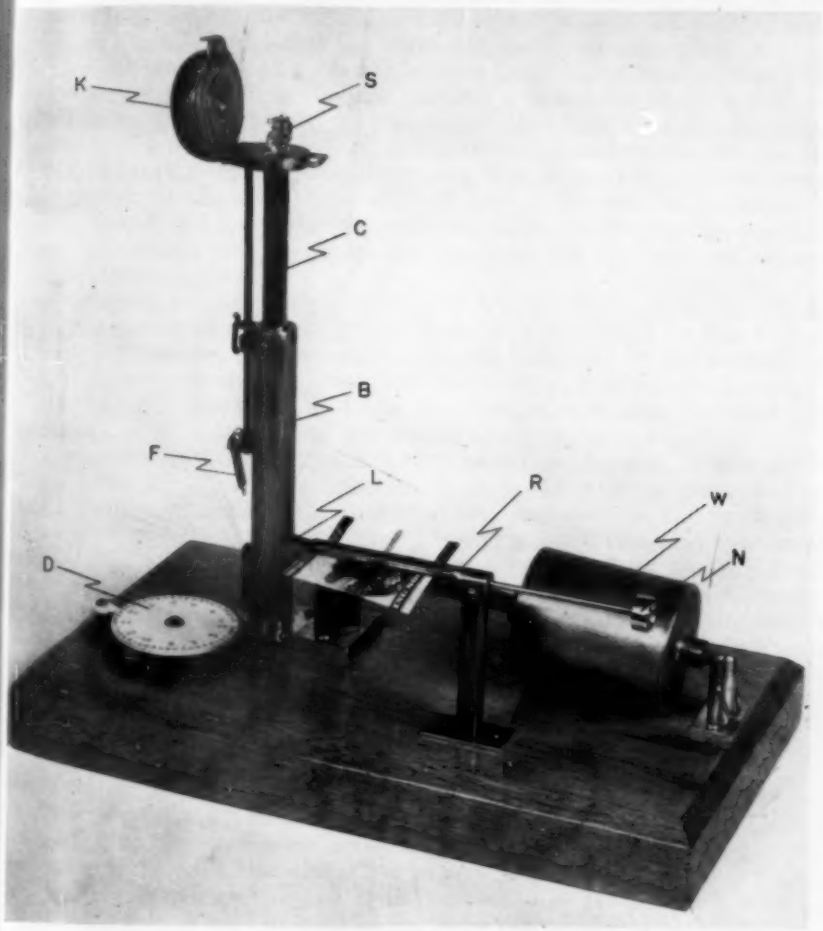

FIGURE 1.—*Crumpling Apparatus.*

raised to the position shown in figure 1, and cap *K* is unlocked. The protruding, crumpled specimen, *S*, is removed and straightened out by hand, after which it is again put in the rolling device, *R* (oriented a quarter turn from the previous position) rolled up, transferred to tube *C*, and crumpled again.

At each crumpling stroke a pivoted finger, *F*, moving downward with tube *C*, engages one of the holes in the counter disk, *D*, and advances the disk one space. The number under the pointer indicates the number of times the specimen has been crumpled.

The counter disk also carries arrows to indicate how to place the specimen in the rolling device. Before a specimen is crumpled, an identifying mark is placed on one edge. The first time the specimen is put in the rolling device, *R*, this mark is placed to the left, at the tip of the fork. Each succeeding time it is advanced a quarter turn. The arrow on the numbered dial, *D*, under the pointer indicates in which one of the four possible positions in the rolling device one is to place the identifying mark on the specimen for the next rolling and crumpling operation.

Five specimens of each paper were crumpled 16 times (4 cycles). The effect of this crumpling treatment was measured by the change in air permeability and in tensile strength produced by the crumpling. When paper is creased or crumpled the interlaced fibers are disturbed, the bonds are loosened, and the disarranged structure becomes less compact, weaker, and more permeable to air under pressure.

Air permeability therefore is a very sensitive measure of this structural change. This measurement was made with a permeameter built to accommodate specimens of the size used in the crumpling apparatus (see footnote 12). Tests were made on identical specimens before and after the specimen had been crumpled 16 times. Each of the 5 crumpled specimens was then cut in the cross direction into 4 strips, and these 20 strips were used in determining the tensile strength of the crumpled paper. The average values for the two tests have been tabulated, and also the percentage retention of the tensile strength after the crumpling treatment (percentage of the normal cross-direction tensile-strength values in table 2).

3. SURFACE WEAR

As already stated, melamine resin was added to some of the papers to see if it would reduce surface disintegration. Tests of these papers, in comparison with the untreated papers, were made with the Taber abrasion instrument,[14] fitted with number CS–17 abrasion wheels, operated under a load of 1 kg each. The conventional circular specimens, clamped at the center, were not stiff enough to remain flat under the action of the abrasion wheels. Octagonal specimens were therefore used, being fastened to the turntable by turning the apexes down over the edge and binding them with a clamping ring.

Six specimens of each of the papers tested were used, half being abraded on one side and half on the other. The values tabulated (table 6) are in each case the average of the six tests.

[14] Paper Trade J. 119, 24 (July 20, 1944).

4. SCUFFING OF WET PAPER

The same papers were tested by rubbing them while wet, until a hole was worn through. An instrument for making such a test was described several years ago.[15] Since then it has been somewhat modified. The abrading surface, originally of rubber, has been replaced by a chromium-plated metal surface, and the clamping device has been improved. The apparatus is illustrated in figure 2.

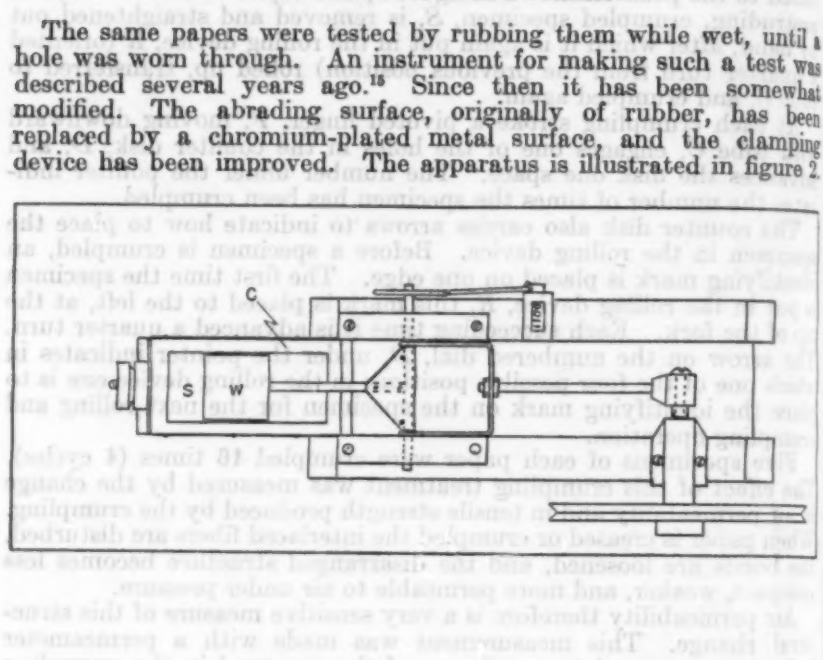

FIGURE 2.—*Sketch of apparatus used to evaluate the resistance of wet paper to scuffing.*

The specimen, *S*, is held at its edges by a rectangular clamping frame, *C*, which serves also as the sides of a shallow basin to hold water placed on the specimen to keep it wet during the test. The clamping frame is held down by a sliding wedge, *R*, moved by turning a thumb

[15] Paper Trade J. 84, TS13 (Jan. 13, 1927).

nut, *T*. A spherical surface, having a radius of curvature of half an inch, shaped on the end of a brass cylinder, *F*, and chromium plated, is moved back and forth in contact with the specimen by a motor-driven crank shaft. Additional pressure is applied by weight *W*. A load of 2.5 pounds was used in these tests. A ratchet counter registers the number of oscillations of the rubbing surface. This test, although not strictly a measure of surface abrasion, inasmuch as a hole is worn entirely through the specimen and the result is in some measure influenced by the strength of the wet paper, appears to indicate major differences in the resistance of papers to scuffing while wet.

The values given (table 6) are averages of 5 tests in each case.

VI. RESULTS OF TESTS

The characteristics of the currency-type papers made are shown by the data[16] in table 2. In this table the papers have been placed in 14 groups according to fiber composition. They consist of machine-finished, waterleaf (unsized) papers; the same surface-sized with glue, tanned with alum (a) or with formaldehyde (f); machine-finished papers containing melamine resin (M); and the same surface-sized with glue, tanned with alum (a).

Paper 3a may be considered the norm of the table as it most resembles the currency paper in use today. All folding-endurance values have been rounded off to the nearest 100 double folds.

All physical properties tabulated, except resistance to tearing, were improved by surface sizing the papers with glue. The data indicate no clear-cut advantage of formaldehyde over alum as tanning agent for the glue. In most instances the folding endurance was greater when the glue was tanned with formaldehyde. The tensile strength was also greater for the papers having a high linen content, but was less for most of the others. Bursting strength and resistance to tearing, however, fared about equally well with the two tanning agents. Stretch at failure was greater in most cases with the alum tanning, which also produced a better closed sheet in all cases (lower air permeability).

In a few of the groups two beating treatments were used. It appears that beating procedure *A* produced a little better paper than did procedure *B*. In two groups the beating (by procedure *B*) was varied in time only. The caroa pulp was benefited by the longer beating period, except that the resistance to tearing was decreased somewhat. The soft-alpha wood pulp, however, benefited little if any by the longer beating time. In all cases the longer beating time, regardless of procedure, resulted in a better closed sheet (lower air permeability).

[16] In previous research (reference 2) at the Bureau on the production of currency paper, the testing was done at 65-percent relative humidity and 70° F. Folding endurance tests at 65-percent relative humidity of a few of the papers made in the present research indicate that these papers are comparable in quality to papers of like composition made in the older research projects.

TABLE 2.—*Properties of experimental currency-type papers*

[All physical tests were made at 50-percent relative humidity and 73° F.]

Designation[1] of papers	Areal weight (half million square inches)[2]	Thickness	Folding endurance in hundred double folds					Tensile strength[3]				Stretch at failure		Resistance to tearing[4]		Bursting strength[5]	Air permeability[6]		Acidity		Glue content	Melamine-resin content
			Schopper		MIT		Composite	Machine	Cross	After 16 crumples		Machine	Cross	Cross	Machine		Before crumpling	After 16 crumples	Cold	Hot		
			Machine[3]	Cross[4]	Machine	Cross				Cross	Retention cross											
			LINEN. BEATEN 12 HOURS BY PROCEDURE *A* (SEE TABLE 1)																			
	lb.	in.×10⁻⁴						kg/cm	kg/cm	kg/cm	%	%	%	g	g	Points	cem	cem	pH	pH	%	%
1	61	36	30	23	19	14	22	7.3	4.1	2.7	67	3.0	8.4	120	117	45	2.0	113	7.2	7.3	.....	.....
1a	61	33	23	28	16	32	25	8.7	4.8	3.5	72	4.5	9.8	96	91	62	0.2	60	6.5	6.8	1.3	.....
1f	62	36	29	36	34	42	35	9.5	5.1	3.7	73	3.8	9.2	98	90	59	.8	75	6.9	7.4	1.9	.....
			COTTON (1 PART) AND LINEN (3 PARTS). BEATEN 12 HOURS BY PROCEDURE *A*																			
2	60	37	34	28	19	14	24	7.1	3.9	2.6	66	2.9	7.2	121	126	46	2.2	146	6.5	7.0	.....	.....
2a	62	36	30	33	29	31	31	8.5	4.9	3.5	71	3.9	10.1	112	107	63	0.2	79	6.5	6.8	1.3	.....
2f	62	34	32	38	37	42	37	8.4	5.2	3.6	69	3.7	12.0	113	101	65	.9	96	6.8	7.5	2.0	.....
			COTTON AND LINEN (EQUAL PARTS). BEATEN 12 HOURS BY PROCEDURE *A*																			
3	61	37	34	28	24	11	24	6.9	3.7	2.4	66	2.7	7.6	132	133	45	2.6	186	6.7	7.3	.....	.....
3a	62	34	28	34	32	28	31	8.4	4.3	3.4	80	4.3	11.6	117	108	60	0.3	105	6.4	6.7	1.3	.....
3f	64	35	36	43	35	30	36	8.5	4.9	3.5	70	3.9	8.8	124	117	65	1.2	130	6.9	7.7	2.0	.....
3M2	61	35	46	52	65	122	71	9.2	5.6	4.3	76	3.9	10.0	107	95	62	1.0	42	6.1	6.0	.....	2.9
3M2a	62	33	41	52	83	104	70	9.7	5.9	5.1	88	4.1	11.4	83	75	70	0.1	28	5.9	6.0	0.9	2.9
			COTTON (3 PARTS) AND LINEN (1 PART). BEATEN 12 HR. BY PROCEDURE *A* (4X BEATEN 8 HR. BY PROCEDURE *B*)																			
4x	62	39	27	16	18	6	17	6.7	3.5	1.9	56	2.2	6.7	141	140	40	5.4	396	7.2	7.1	.....	.....
4xa	65	38	36	50	22	26	34	8.9	5.0	3.3	67	4.0	9.7	132	139	63	1.0	177	6.0	6.3	1.7	.....

COTTON (3 PARTS) AND LINEN (1 PART). BEATEN 12 HR. BY PROCEDURE *A* (4x BEATEN 8 HR. BY PROCEDURE *B*)

4x	62	39	27	16	18	6	17	6.7	3.5	1.9	56	2.2	6.7	141	140	40	5.4	396	7.2	7.1	------	------
4xa	66	38	36	50	22	26	34	8.9	5.0	3.3	67	4.0	9.7	132	139	63	1.0	177	6.0	6.3	1.7	------
4	61	38	32	14	25	8	20	6.5	3.6	2.1	57	2.6	7.8	142	138	43	2.9	293	6.4	6.6	------	------
4a	64	36	35	37	37	23	33	8.9	4.9	3.2	65	4.0	9.6	126	122	62	0.3	142	6.3	6.8	1.3	------
4f	62	37	36	29	47	28	35	8.0	4.7	3.1	66	3.9	9.6	109	114	60	1.4	209	6.8	7.6	2.0	------

COTTON. BEATEN 12 HR. BY PROCEDURE *A* (5x BEATEN 8 HR. BY PROCEDURE *B*)

5x	61	39	31	18	14	8	18	6.1	3.6	1.9	54	2.2	6.9	142	156	34	5.5	442	7.2	7.6	------	------
5xa	65	39	37	59	27	32	39	8.8	5.0	3.4	68	3.7	9.4	130	145	64	0.8	168	6.0	6.2	1.9	------
5	62	38	33	20	24	9	22	6.3	3.6	2.0	56	2.5	7.6	154	156	40	3.1	329	6.6	7.2	------	------
5a	66	35	28	30	37	22	29	8.5	5.0	3.1	63	4.7	10.8	135	134	60	0.3	169	6.1	6.2	1.3	------
5f	64	36	40	39	36	28	36	8.3	4.9	2.9	59	3.7	9.7	118	125	66	1.7	275	6.7	7.6	2.1	------
5M2	60	36	44	53	80	93	68	9.3	5.5	4.6	83	4.0	10.1	99	113	65	1.3	87	5.7	5.7	------	2.5
5M2a	61	33	44	56	88	119	77	9.9	6.2	5.4	87	4.3	11.6	90	85	80	0.1	57	5.6	6.0	1.0	2.5

CAROA. BEATING PROCEDURE *B*, 9 HOURS (6x, 7 HOURS)

6x	62	49	18	20	17	16	18	6.6	3.8	2.9	77	3.3	9.5	187	175	45	17.4	1,192	8.1	7.6	------	------
6	62	43	22	32	20	18	23	7.6	4.3	3.2	74	3.8	11.7	163	164	53	8.2	509	5.8	4.8	------	------
6a	62	42	21	32	26	32	28	8.2	4.7	4.1	87	4.7	12.1	143	144	67	0.7	269	5.4	4.7	2.4	------

COTTON AND CAROA (EQUAL PARTS). BEATEN 9 HOURS BY PROCEDURE *B*

7	64	39	29	23	18	9	20	7.1	3.9	2.5	64	3.4	10.5	146	156	51	4.0	287	5.7	4.6	------	------
7a	65	38	35	31	26	21	28	8.5	4.5	3.3	75	4.0	11.3	131	120	63	0.2	147	5.4	4.8	1.4	------

SISAL. BEATEN 7 HOURS BY PROCEDURE *B*

8	61	41	16	16	11	8	13	6.3	3.4	2.1	61	3.9	10.8	144	147	39	5.3	978	6.4	5.4	------	------
8a	65	41	15	22	13	16	17	7.1	4.1	2.9	71	3.1	11.2	120	124	51	0.5	484	5.9	5.2	2.3	------

See footnotes at end of table.

TABLE 2.—*Properties of experimental currency-type papers*—Continued

Designation [1] of papers	Areal weight (half million square inches) [2]	Thickness	Folding endurance in hundred double folds					Tensile strength [5]				Stretch at failure		Resistance to tearing [6]		Bursting strength [7]	Air permeability [8]		Acidity		Glue content	Melamine-resin content
			Schopper		MIT		Composite	Machine	Cross	After 16 crumples		Machine	Cross	Cross	Machine		Before crumpling	After 16 crumples	Cold	Hot		
			Machine [3]	Cross [4]	Machine	Cross				Cross	Retention cross											
			COTTON AND SISAL (EQUAL PARTS). BEATEN 8 HOURS BY PROCEDURE *B*																			
	lb.	*in.* × 10^{-4}						*kg/cm*	*kg/cm*	*kg/cm*	%	%	%	*g*	*g*	*Points*	*csm*	*csm*	pH	pH	%	%
9	61	38	20	20	10	7	14	6.5	3.6	2.1	57	3.2	8.9	148	156	38	4.0	355	6.1	5.1	------	------
9a	63	39	24	23	12	14	18	6.9	4.0	2.6	65	3.2	8.9	128	139	48	0.4	215	5.7	5.0	1.7	------
			HARD-ALPHA WOOD PULP. BEATEN 9 HOURS BY PROCEDURE *B*																			
10	59	37	15	8	17	26	17	6.3	3.1	1.6	50	2.0	7.1	76	72	37	17.9	2,438	6.4	6.4	------	------
10a	64	37	14	12	14	14	14	8.7	4.6	2.9	64	2.9	9.5	65	57	53	3.1	1,404	5.9	5.8	2.3	------
10f	62	34	12	13	13	10	12	7.7	4.3	2.6	59	2.4	7.7	66	57	49	7.8	1,867	6.4	6.4	2.7	------
10M1	60	37	18	13	16	12	15	7.6	3.8	2.5	67	2.4	6.8	68	61	44	17.2	1,672	6.3	6.1	------	2.7
10M1a	64	36	10	15	22	25	18	8.5	5.1	3.3	64	2.6	8.5	57	51	55	2.9	1,107	6.1	6.0	1.7	2.7
10M2	60	35	17	20	9	14	15	8.3	4.9	3.4	70	2.5	8.7	56	53	52	8.6	695	6.0	5.8	------	3.0
10M2a	61	33	14	17	33	41	26	8.9	5.4	3.7	69	2.8	9.8	53	48	60	1.3	543	5.7	5.9	1.6	3.0
10M3	59	33	18	20	29	42	27	8.7	4.7	3.5	75	2.9	8.6	56	53	51	3.8	488	4.8	4.9	------	2.5
10M3a	62	33	15	18	34	47	29	8.7	5.3	3.9	74	3.0	10.6	51	47	59	0.2	383	5.0	5.1	1.4	2.5
			COTTON AND HARD-ALPHA WOOD PULP (EQUAL PARTS). BEATEN 13 HOURS BY PROCEDURE *A* (11X, 9 HOURS BY PROCEDURE *B*)																			
11x	60	38	21	13	12	5	13	6.0	3.2	1.9	60	2.1	6.6	116	130	34	5.0	736	6.7	7.3	------	------
11xa	66	40	24	30	19	22	24	8.0	5.0	3.1	61	3.7	9.6	113	119	56	0.5	415	6.0	5.2	1.6	------
11	60	38	23	15	13	5	14	6.2	3.5	1.9	53	3.0	6.9	128	131	32	3.7	688	6.5	6.8	------	------
11a	62	35	22	22	18	13	19	7.3	4.3	2.7	63	2.9	8.5	112	103	50	0.3	396	6.1	6.1	1.5	------
11f	64	38	22	29	24	21	24	8.3	4.5	3.0	66	2.9	7.5	107	105	55	1.7	521	6.6	6.9	2.1	------
			SULFATE WOOD PULP. BEATEN 9 HOURS BY PROCEDURE *B*																			
12	60	38	15	18	15	16	16	9.3	4.9	3.0	62	2.4	8.5	92	76	52	2.5	1,087	7.3	7.2	------	------
12a	62	36	11	16	18	21	17	8.9	5.4	3.9	72	2.7	9.8	80	73	59	0.3	740	6.7	7.1	1.5	------

SULFATE WOOD PULP. BEATEN 9 HOURS BY PROCEDURE *B*

12	60	38	15	18	15	16	16	9.3	4.9	3.0	62	2.4	8.5	92	76	52	2.5	1,087	7.3	7.2	------	------
12a	62	36	11	16	18	21	17	8.9	5.4	3.9	72	2.7	9.8	80	73	59	0.3	740	6.7	7.1	1.5	------

SULFITE WOOD PULP. BEATEN 7 HOURS BY PROCEDURE *B*

13	60	37	8	7	6	4	6	6.6	3.6	1.5	41	1.6	5.2	62	61	34	12.1	2,841	6.6	6.5	------	------
13a	63	36	7	10	12	9	10	8.1	5.0	2.7	55	2.2	7.2	54	50	51	3.0	1,771	6.3	6.3	1.9	------
13M3	61	35	9	12	25	20	17	8.7	4.9	3.1	63	2.9	7.3	53	47	45	3.6	859	5.2	5.2	------	2.5
13M3a	62	33	7	10	17	22	14	8.9	5.3	3.3	63	2.4	8.3	47	45	49	0.2	639	5.5	5.5	0.9	2.5

SOFT-ALPHA WOOD PULP. BEATING PROCEDURE *B*, 8 HOURS (14X, 12 HOURS)

14x	60	37	3	2	2	1	2	5.1	2.9	1.4	49	2.2	7.2	57	59	28	11.3	1,417	6.9	7.1	------	------
14xa	64	37	4	5	7	6	6	7.1	4.3	2.3	54	3.0	6.9	54	56	44	2.0	939	5.8	5.8	2.5	------
14	59	36	5	2	2	1	3	5.5	2.4	1.0	42	2.2	4.8	73	70	31	41.2	3,382	6.3	6.2	------	------
14a	62	36	6	6	7	6	6	6.7	4.1	2.3	56	2.5	7.6	55	51	48	18.9	2,207	6.0	5.9	2.7	------
14M3	60	37	10	13	22	16	15	7.0	4.7	3.1	67	2.9	8.2	55	52	50	15.5	777	5.2	5.2	------	2.7
14M3a	63	36	8	11	21	27	17	8.2	5.0	3.5	71	3.2	8.1	52	48	57	3.4	624	5.4	5.4	1.7	2.7

[1] The papers are numbered by groups (14 in all), according to fiber composition. An "*x*" following the numeral indicates a subgroup having beating treatment different from that of the remainder of the group. Surface-sized papers are indicated by a final "*a*" or "*f*", signifying that the glue sizing was tanned with alum (*a*) or with formaldehyde (*f*). "*M*" followed by 1, 2, or 3 indicates that the paper contains melamine resin added by method 1, 2, or 3:

Method 1.—Melamine resin was added to the stock in the machine chest. The stock was run on the paper machine at a pH of 6.9 (obtained by buffering with soda ash).

Method 2.—Melamine resin was added continuously to the stock between screen and head box.

Method 3.—The stock was made acid in the chest with alum. Melamine resin was added continuously to the stock between screen and head box.

[2] Weight of a hypothetical ream of 500 sheets, each measuring 25 by 40 inches, that is, the weight of half a million square inches of paper.

[3] Machine direction, or with the grain of the paper.

[4] Cross direction, or against the grain.

[5] Tensile strength was measured by breaking a strip of paper 1.5 cm wide and 10 cm long between clamps. The usual practice is to report the breaking force for the full width, kilograms per 1.5-cm width, but the data for this table have been reduced to unit width (kg/cm). The tensile data include strength in the cross direction after the paper had been crumpled 16 times, and the percentage retention of strength after the crumpling treatment. See text for method of crumpling.

[6] In tabulating the data for resistance to tearing, the designated directions tested are reversed to make the data comparable with those of the other tests. In paper-testing usage the direction tested is generally designated as the principal direction of orientation of the fibers ruptured, but in the tearing test (Elmendorf), according to official nomenclature, the direction designated is the direction of the tear, which is oriented 90 degrees to the principal direction of the fibers ruptured.

[7] Determined as bursting pressure in pounds per square inch by a particular apparatus and procedure (TAPPI T403m). Because the bursting pressure depends on the area tested, and because of the chance of confusing the pressure unit with the conventional unit of strength of materials, it has become customary to designate the unit of bursting strength as "points".

[8] The unit of air permeability, *csm*, is an abbreviation of cubic centimeters of air flowing in a second through a square meter of the material under unit pressure difference (1 g/cm^2).

The addition of melamine resin substantially improved all physical properties listed in the table, except resistance to tearing, which was decreased. A possible exception is the paper 10M1, to which melamine resin was added in the machine chest by method 1, only moderate improvement being apparent in this paper in comparison with its companion made without melamine resin. It is apparent also that surface sizing with glue, in addition to the adding of melamine resin, still further improved the quality of the paper, with the exception of resistance to tearing. Addition of melamine resin to the cotton and to the cotton-linen mixture, and subsequent surface sizing, nearly doubled the tensile strength and bursting strength, and increased the wearing quality (folding endurance and strength after crumpling) two- to threefold, but lowered the resistance to tearing about a third.

From table 2 it appears that, whereas the MIT folding endurance is usually lower than the Schopper for plain papers, it increases more rapidly than does the Schopper folding endurance as a result of surface sizing. When melamine resin is added the MIT value becomes considerably greater than the Schopper value in most cases. As the two kinds of folding-endurance tests do not agree very well, a composite value, which is the average of both tests in both directions, is also included in table 2.

To help in assessing the worth of materials that might be substituted for linen fiber in currency-type paper, table 3 has been prepared, in which the values for a given property have been expressed as percentages of the corresponding value of paper 3a. The composite folding endurance is used, and the values for stretch, tensile strength, and resistance to tearing were calculated from the mean value of the two directions of the papers in each instance. This table permits the paper-making properties of the various fibers studied to be compared with those of linen fiber, in terms of the requirements of currently used currency paper, represented by paper 3a.

By currency-paper standards cotton makes a good paper, except that it is somewhat soft and lacking in a kind of intangible superiority universally associated with currency and bank-note papers containing linen fiber. The data in table 3 indicate that the cotton paper is a very excellent product, except for a too open and "soft" structure, reflected in a comparatively low air resistance after the laboratory wearing treatment by crumpling. The caroa paper is also of superior quality, except that its air resistance is lower still.

It is observed that this tendency toward a "soft" structure produced by most of the fibers appears to be counteracted by the addition of melamine resin. The improvement is remarkable in the cotton paper, 5M2a, and most of the other properties are enhanced also. No papers were made with caroa fiber and melamine resin in combination. The melamine resin is not an unalloyed advantage, however, inasmuch as it tends to reduce the resistance to tearing. Both cotton and caroa papers are very resistant to tearing and can stand considerable loss in this respect without becoming inferior to currently used currency paper.

TABLE 3.—*Properties*[1] *of single-fiber-component papers expressed as percentage of the corresponding value for paper*[2] *5a*

Designation[3] of papers	Kind of fiber	Composite folding endurance	After 16 crumples		Stretch	Bursting strength	Tensile strength	Resistance to tearing
			Tensile strength	Air resistance				
PAPERS SURFACE SIZED WITH GLUE								
		%	%	%	%	%	%	%
1a	Linen	81	103	175	95	103	108	83
5a	Cotton	93	91	62	101	100	109	120
6a	Caroa	90	121	39	107	112	104	128
8a	Sisal	55	85	22	85	85	90	109
10a	Hard alpha	45	85	7	75	88	106	58
12a	Sulfate	55	115	14	74	96	116	68
13a	Sulfite	32	79	6	57	85	106	46
14a	Soft alpha	19	68	5	62	80	88	47
PAPERS CONTAINING MELAMINE RESIN AND SURFACE SIZED WITH GLUE								
5M2a	Cotton	248	130	184	100	133	131	78
10M3a	Hard alpha	94	115	27	85	98	110	44
13M3a	Sulfite	45	97	16	64	82	115	41
14M3a	Soft alpha	55	103	17	72	95	107	44
PAPERS CONTAINING MELAMINE RESIN AND NOT SURFACE SIZED								
5M2	Cotton	219	135	121	90	108	120	95
10M3	Hard alpha	87	103	22	72	85	106	49
13M3	Sulfite	55	91	12	66	75	109	45
14M3	Soft alpha	48	91	14	70	83	96	48
PAPERS CONTAINING NO MELAMINE RESIN AND NOT SURFACE SIZED								
5	Cotton	71	59	32	62	67	80	139
10	Hard alpha	55	47	4	54	62	74	66
13	Sulfite	19	44	4	41	57	82	55
14	Soft alpha	10	29	3	46	52	61	64

[1] The percentage values given are the mean for the machine and cross directions. The folding-endurance values are the mean of MIT and Schopper values in both directions.
[2] The present standard type of currency paper composed of equal parts of linen and cotton fibers.
[3] The numbering is the same as that in table 2, the "M" signifying the addition of melamine resin.

It seems probable therefore that, in case of necessity, a judicious combination of cotton, caroa, and melamine resin might be substituted for linen fiber in currency paper without loss of quality of the paper, provided it did not in some unforeseen manner displace the nice balance of characteristics of linen-content paper associated with the rather complex process of printing and production of paper currency. The wood fibers do not appear suitable for use in currency-type papers, nor does sisal seem promising.

Some special tests were made on the machine-finished papers containing melamine resin and the companion papers made without melamine resin. A brief statement of the findings, which are not tabulated, follows. The melamine resin decreased the opacity slightly, about 4 percent on the average. It appeared to increase the water resistance slightly (measured by the dry-indicator test and the curl

test, both of which are described in TAPPI methods), but the papers containing the mealmine resin were still water-leaf. The grease resistance also was increased slightly. In neither case, however, was the improvement of any consequence. Expansivity was not altered significantly by the addition of melamine resin.

These papers were also aged for 72 hours at 100° C. and the deterioration, evaluated by the change in folding endurance, is shown in table 4. The pH of all the papers listed in this table was greater than 5 (see table 2). The data obtained indicate that the papers containing melamine resin compare favorably in stability with similar papers containing no melamine resin, provided the acidity is not greater than the maximum allowable for good stability of papers in general, that is, provided the pH is not less than 5.

TABLE 4.—*Comparison of the effects of accelerated aging for 72 hours at 100° C on papers containing melamine resin and on their companion papers made without the resin*

Designation [1] of papers	Ratio of Schopper folding endurance after aging to that before aging	
	Machine direction	Cross direction
COTTON AND LINEN		
3	0.91	1.04
3M2	.81	0.94
COTTON		
5	1.03	0.95
5M2	0.82	1.00
HARD-ALPHA WOOD PULP		
10	0.73	0.75
10M2	.71	.80
SULFITE WOOD PULP		
13	0.75	0.86
13M3	.78	.83

[1] The numbering is the same as that in table 2, the "M" signifying the addition of melamine resin.

TABLE 5.—*Improvement in strength of wet paper resulting from addition of melamine resin*

Designation [1] of paper	Strength ratio, wet [2] to dry				
	Bursting strength	Tensile strength		Tearing resistance	
		Machine direction	Cross direction	Cross direction	Machine direction
COTTON AND LINEN					
3	0.06	0.03	0.04	0.42	0.40
3M2	.73	.40	.42	1.45	1.32
COTTON					
5	0.08	0.03	0.06	0.42	0.31
5M2	.81	.47	.55	1.70	1.27
HARD-ALPHA WOOD PULP					
10	0.09	0.03	0.04	0.62	0.49
10M1	.35	.22	.37	1.71	1.52
10M2	.52	.39	.44	1.09	0.81
10M3	.46	.36	.40	1.86	1.70
SULFITE WOOD PULP					
13	0.09	0.03	0.04	0.95	0.71
13M3	.47	.31	.36	1.51	1.26
SOFT-ALPHA WOOD PULP					
14	0.05	0.02	0.06	0.48	0.44
14M3	.46	.42	.44	1.25	1.08

[1] The numbering is the same as that in table 2, the "M" signifying the addition of melamine resin.
[2] The wet papers had been soaked in water for 24 hours before they were tested.

TABLE 6.—*Improvement in surface-wear resistance imparted by melamine resin in the paper, and by glue surface sizing*

Designation [1] of papers	Materials added to improve the quality of the surface	Resistance to abrasion		
		Taber (dry)	NBS (wet)	
			Machine direction	Cross direction
	COTTON AND LINEN			
		Rev/mg	*Oscillations*	*Oscillations*
3	None	6	9	9
3a	Surface sizing (glue, alum)	18	19	17
3M2	Melamine resin	20	625	560
3M2a	Melamine resin and surface sizing	21	671	733
	COTTON			
5	None	2	10	9
5a	Surface sizing	25	20	21
5M2	Melamine resin	12	725	560
5M2a	Melamine resin and surface sizing	32	898	770
	HARD-ALPHA WOOD PULP			
10	None	4	6	5
10a	Surface sizing	14	30	21
10M2	Melamine resin	14	218	161
10M2a	Melamine resin and surface sizing	18	289	273
	SULFITE WOOD PULP			
13	None	3	7	6
13a	Surface sizing	10	59	45
13M3	Melamine resin	11	128	96
13M3a	Melamine resin and surface sizing	14	160	132
	SOFT-ALPHA WOOD PULP			
14	None	3	4	1
14a	Surface sizing	12	25	7
14M3	Melamine resin	11	255	227
14M3a	Melamine resin and surface sizing	17	335	260

[1] The numbering is the same as that in table 2, the "M" signifying the addition of melamine resin.

The use of melamine resin in paper is ordinarily for the primary purpose of increasing the strength of the paper when wet. Paper currency is of course sometimes handled when wet. The improvement in the strength of wet paper imparted by melamine resin is shown in table 5. The improvement is very striking in all of the experimental papers containing the resin.

As previously stated, one of the chief reasons for adding melamine resin to some of these experimental papers was to see if it would improve the surface, and lessen its tendency to scuff, crack, or wear away. Table 6 shows the resistance to abrasion of both dry paper and wet paper. Although both types of test are rather erratic, the differences are great enough to indicate that the melamine resin does help to improve the resistance of the surafce to abrasion.

The abrasion tests on the dry paper indicate that the glue surface sizing and the melamine resin are about equally effective in minimizing the ordinary surface wear. The two together, however, give even better results.

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HEATS OF FORMATION, HYDROGENATION, AND COMBUSTION OF THE MONOOLEFIN HYDROCARBONS THROUGH THE HEXENES, AND OF THE HIGHER 1-ALKENES, IN THE GASEOUS STATE AT 25° C [1]

By Edward J. Prosen and Frederick D. Rossini

ABSTRACT

For ethylene, propylene, the four butenes, the six pentenes, and the 17 hexenes, and all the higher 1-alkene hydrocarbons, in the gaseous state at 25° C, values are given for the heats of formation (from the elements solid carbon (graphite) and gaseous hydrogen), the heats of hydrogenation in the gaseous state, and the heats of combustion (in oxygen to form gaseous carbon dioxide and liquid water). The values for 2 of the pentenes, 14 of the 17 hexenes, and all the higher 1-alkene hydrocarbons, were calculated by a method involving correlation of the heat of hydrogenation with structure and the use of constants evaluated from the available experimental data on 4 butenes, 4 pentenes, 3 hexenes, and 1 heptene.

CONTENTS

	Page
I. Introduction	269
II. Units, constants, uncertainties	270
III. Data used in the calculations	270
IV. Method of calculation	271
V. Results	273
VI. References	275

I. INTRODUCTION

In a previous report [1] [2] values were given for the heats of formation of the monoolefin hydrocarbons from ethylene through the pentenes in the gaseous state. At that time, the data on the heats of hydrogenation of the higher monoolefins [2, 3] could not be utilized for calculating heats of formation because of the lack of reliable experimental data on the corresponding paraffin hydrocarbons. Since then new data on the paraffin hydrocarbons above the pentanes have become available [4, 5, 6, 7, 8]. The present paper presents (a) revised values for the monoolefins through the pentenes, changed on account of slight revisions in the selected "best" values for heats of formation of water and carbon dioxide [9, 10] and of improved values of specific heat [11, 12] for converting to 25° C the heats of

[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons."

[2] Figures in brackets indicate the literature references at the end of this paper.

hydrogenation [2, 3, 18] measured at 82° C, and (b) new values for the hexenes and the higher 1-alkene hydrocarbons, utilizing data on specific heat and heat of hydrogenation of the monoolefins and new data on the heats of formation of the paraffins. For these compounds, values of the heats of formation, hydrogenation, and combustion are given for the gaseous state at 25° C. The values for 2 of the pentenes, 14 of the hexenes, and all the higher 1-alkene hydrocarbons were calculated by a method involving correlation of the heat of hydrogenation with structure and the use of constants evaluated from the available data on 4 butenes, 4 pentenes, 3 hexenes and 1 heptene.

II. UNITS, CONSTANTS, UNCERTAINTIES

The unit of energy upon which the values presented in this paper are based is the international joule determined by standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau. Conversion to the conventional thermochemical calorie is made by means of the relation [13]

4.1833 international joules=1 calorie.

The molecular weights of hydrogen, oxygen, and carbon were taken as 1.0080, 16.0000, and 12.010, respectively, from the 1941 table of International Atomic Weights [14].

The uncertainties assigned to the various quantities dealt with were derived, where possible, by a method previously described [15]. In other cases, reasonable estimates of the uncertainties were made.

III. DATA USED IN THE CALCULATIONS

The following data were used in the calculations:

Heat of formation of carbon dioxide at 25° C [9].

Heat of formation of water at 25° C [10].

Heats of combusion of ethylene and propylene at 25° C [16].

Heats of hydrogenation, at 82° C, of ethylene, propylene, 1-butene, *cis*-2-butene, *trans*-2-butene, isobutene, 2-pentene (mixture of *cis* and *trans* isomers), 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, and 1-heptene [2, 3, 17, 18].

Heats of formation of the paraffin hydrocarbons at 25° C [8].

Values of $\Delta H°_{355}-\Delta H°_{298.16}$ for the reaction of hydrogenation of the appropriate monoolefin hydrocarbons calculated statistically from spectroscopic and other molecular data [11, 12].

IV. METHOD OF CALCULATION

For ethylene and propylene, values of the heat of formation at 25° C were calculated both from (a) the data on the heat of combustion of the olefin [16] and the heats of formation of water [10] and carbon dioxide [9], all at 25° C, and (b) the data on the heat of hydrogenation of the olefin at 82° C [17, 18], corrected to 25° C with appropriate values of the change of the heat content with the change of temperature [10, 11, 12, 21, 22, 23], and the recently published selected "best" value for the heat of formation of the corresponding paraffin [8]. The resulting values were weighted inversely as the square of their assigned uncertainties to obtain the selected best values for the heats of formation of ethylene and propylene. The selected best values for the heats of hydrogenation of ethylene and propylene were then taken as the appropriate differences in the selected best values for the heats of formation of ethylene and ethane and propylene and propane.

The values for the heats of formation at 25° C of 1-butene, *cis*-2-butene, *trans*-2-butene, 2-methylpropene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene were calculated from the heats of hydrogenation at 82° C [2, 3, 18], corrected to 25° C with appropriate values of the change of heat content with change of temperature, combined with the selected best values of the heats of formation of the corresponding paraffins [8]. The values for *cis*-2-pentene and *trans*-2-pentene were similarly obtained by using the data on the heat of hydrogenation at 82° C of a mixture of *cis*-and *trans*-2-pentene [2], and assuming the relative amounts of the two isomers to be as given by Kistiakowsky, et al. [2] and the difference in their heats of hydrogenation at 82° C to be the same as the difference between *cis*-2-butene and *trans*-2-butene at 82° C.

The values for the 14 hexenes for which no experimental data are available were calculated by a method involving correlation of the heat of hydrogenation with molecular structure, as follows:

The monoolefin hydrocarbons were divided into classes according to the number and location of the alkyl substituents, R, on the double-bond carbon atoms, as has previously been done in connection with other properties [19, 20].

Table 1 lists the several types of monoolefins, together with the values selected for their heats of hydrogenation. The values were selected as follows:

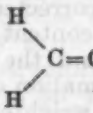
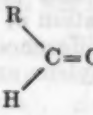
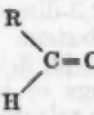
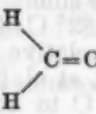
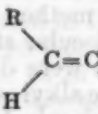
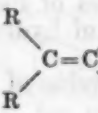
For type I, $H_2C=CHR$, the value of the heat of hydrogenation at 25° was taken as

$$(H_2C=CHR)(gas)+H_2(gas)=(H_3C-CH_2R)(gas) \qquad (1a)$$

$$\Delta H^\circ_{298.16}=-30.00 \pm 0.40 \text{ kcal/mole}, \qquad (1b)$$

which is a rounded average of the following four values based on experiment: 1-butene, -30.092 ± 0.081; 3-methyl-1-butene, -29.995 ± 0.082; 3,3-dimethyl-1-butene, -30.103 ± 0.153; 1-heptene, -29.876 ± 0.100, kcal/mole.

TABLE 1.—*Values of the heats of hydrogenation selected for the several classes of monoolefin hydrocarbons*

Type	Structure	Selected value of $\Delta Hh°_{298.16}$
		Kcal/mole
I		−30.00 ±0.40
IIc		−28.40 ±0.50
IIt		−27.40 ±0.50
III		−28.10 ±0.50
IV		−26.70 ±0.50
V		

For type IIc, RHC=CHR (*cis*), the value of the heat of hydrogenation at 25° C was taken as

$$(\mathrm{RHC{=}CHR})(cis)(\mathrm{gas})+\mathrm{H_2(gas)}=(\mathrm{RH_2C{-}CH_2R})(\mathrm{gas}), \quad (2a)$$

$$\Delta H°_{298.16}=-28.40 \pm 0.50 \text{ kcal/mole}, \quad (2b)$$

which is based on the experimental value for *cis*-2-butene, supported by the data on 2-pentene (*cis*+*trans*).

For type IIt, RHC=CHR (*trans*), the value of the heat of hydrogenation at 25° C was taken as

$$(\mathrm{RHC{=}CHR})(trans)(\mathrm{gas})+\mathrm{H_2(gas)}=(\mathrm{RH_2C{-}CH_2R})(\mathrm{gas}) \quad (3a)$$

$$\Delta H^\circ_{298.16}=-27.40\ \pm 0.50\ \text{kcal/mole}, \quad (3b)$$

which is based on the experimental value for *trans*-2-butene, supported by the data on 2-pentene (*cis*+*trans*).

For type III, $H_2C{=}CR_2$, the value of the heat of hydrogenation at 25° C was taken as

$$(\mathrm{H_2C{=}CR_2})(\mathrm{gas})+\mathrm{H_2(gas)}=(\mathrm{H_3C{-}CHR_2})(\mathrm{gas}), \quad (4a)$$

$$\Delta H^\circ_{298.16}=-28.10\ \pm 0.50\ \text{kcal/mole}, \quad (4b)$$

which is based on the experimental values for the following three compounds: Isobutene, −28.109 ±0.80; 2-methyl-1-butene, −28.240 ±0.122; 2,3-dimethyl-1-butene, −27.713 ±0.124 kcal/mole.

For type IV, $RHC{=}CR_2$, the value of the heat of hydrogenation at 25° C was taken as

$$(\mathrm{RHC{=}CR_2})(\mathrm{gas})+\mathrm{H_2(gas)}=(\mathrm{RH_2C{-}CHR_2})(\mathrm{gas}) \quad (5a)$$

$$\Delta H^\circ_{298.16}=-26.70\ \pm 0.50\ \text{kcal/mole}, \quad (5b)$$

which is based on the experimental value for 2-methyl-2-butene, −26.745 ±0.082 kcal/mole.

As there is only one hexene of type V, 2,3-dimethyl-2-butene, and as experimental data for it are available, no value for it was required to be selected for further calculation.

V. RESULTS

The results of the calculations are presented in table 2, which gives the values for the heats of formation, hydrogenation, and combustion of the monoolefin hydrocarbons in the gaseous state at 25° C. For the 1-alkenes above 1-pentene, the tabulated values were calculated from the following equations:

For the heat of formation—

$$n\mathrm{C\ (solid,\ graphite)}+n\mathrm{H_2\ (gas)}=\mathrm{C_nH_{2n}\ (gas)} \quad (6a)$$

$$\Delta H^\circ_{298.16}=19.592-4.926n\pm(0.3248-0.03884n+0.002893n^2)^{1/2}\ \text{kcal/mole};\ n>5. \quad (6b)$$

For the heat of hydrogenation—

$$\mathrm{C_nH_{2n}\ (gas)}+\mathrm{H_2\ (gas)}=\mathrm{C_nH_{2n+2}\ (gas)} \quad (7a)$$

$$\Delta H^\circ_{298.16}=-30.00\pm 0.40\ \text{kcal/mole};\ n>5 \quad (7b)$$

For the heat of combustion—

$$C_nH_{2n}\ (gas)+\frac{3n}{2}\ O_2\ (gas)=n\ CO_2\ (gas)+nH_2O\ (liquid) \quad (8a)$$

$$\Delta H°_{298.16}=-19.592-157.443n\pm(0.3248-0.03884n+0.003102n^2)^{1/2}\ kcal/mole;\ n>5 \quad (8b)$$

Equations 7a and 7b correspond to eq 1a and 1b of this report. Equations 6a and 6b were obtained by combining eq 7a and 7b of this report with eq 5 and 6 from [8]. Equations 8a and 8b were obtained by appropriately combining with eq 6a and 6b the equations for the heats of formation of water and carbon dioxide.

TABLE 2.—*Heats of formation, hydrogenation, and combustion of the monoolefin hydrocarbons through the hexenes, and of the higher 1-alkene hydrocarbons, in the gaseous state at 25° C*

Compound (gas)	Formula	Heat of formation [1] $\Delta Hf°$	Heat of hydrogenation [2] $\Delta H\text{h}°$	Heat of combustion [3] $-\Delta Hc°$
		Kcal/mole	*Kcal/mole*	*Kcal/mole*
Ethene (ethylene)	C_2H_4	+12.496 ±0.066	−32.732 ±0.133	337.234 ±0.072
Propene (propylene)	C_3H_6	+4.879 ± .122	−29.699 ± .181	491.987 ± .129
1-Butene	C_4H_8	+0.280 ± .196	−30.092 ± .081	649.757 ± .204
cis-2-Butene	C_4H_8	−1.362 ± .196	−28.450 ± .080	648.115 ± .204
trans-2-Butene	C_4H_8	−2.405 ± .196	−27.407 ± .080	647.072 ± .204
2-Methylpropene (isobutene)	C_4H_8	−3.343 ± .182	−28.109 ± .080	646.134 ± .191
1-Pentene	C_5H_{10}	−5.00 ± .43	−30.00 ± .400	806.85 ± .44
cis-2-Pentene	C_5H_{10}	−6.51 ± .26	−28.491 ± .201	805.34 ± .27
trans-2-Pentene	C_5H_{10}	−7.59 ± .26	−27.410 ± .201	804.26 ± .27
2-Methyl-1-butene	C_5H_{10}	−8.68 ± .23	−28.240 ± .182	803.17 ± .24
3-Methyl-1-butene	C_5H_{10}	−6.92 ± .22	−29.935 ± .082	804.93 ± .23
2-Methyl-2-butene	C_5H_{10}	−10.17 ± .22	−26.745 ± .082	801.68 ± .23
1-Hexene	C_6H_{12}	−9.96 ± .44	−30.00 ± .40	964.23 ± .45
cis-2-Hexene	C_6H_{12}	−11.56 ± .53	−28.40 ± .50	962.66 ± .54
trans-2-Hexene	C_6H_{12}	−12.56 ± .53	−27.40 ± .50	961.66 ± .54
cis-3-Hexene	C_6H_{12}	−11.56 ± .53	−28.40 ± .50	962.66 ± .54
trans-3-Hexene	C_6H_{12}	−12.56 ± .53	−27.40 ± .50	961.66 ± .54
2-Methyl-1-pentene	C_6H_{12}	−13.56 ± .56	−28.10 ± .50	960.65 ± .57
3-Methyl-1-pentene	C_6H_{12}	−11.02 ± .46	−30.00 ± .40	963.20 ± .47
4-Methyl-1-pentene	C_6H_{12}	−11.66 ± .47	−30.00 ± .40	962.56 ± .48
2-Methyl-2-pentene	C_6H_{12}	−14.96 ± .56	−26.70 ± .50	959.26 ± .57
cis-3-Methyl-2-pentene	C_6H_{12}	−14.32 ± .55	−26.70 ± .50	959.90 ± .56
trans-3-Methyl-2-pentene	C_6H_{12}	−14.32 ± .55	−26.70 ± .50	959.90 ± .56
cis-4-Methyl-2-pentene	C_6H_{12}	−13.26 ± .56	−28.40 ± .50	960.96 ± .57
trans-4-Methyl-2-pentene	C_6H_{12}	−14.26 ± .56	−27.40 ± .50	959.96 ± .57
2-Ethyl-1-butene	C_6H_{12}	−12.92 ± .55	−28.10 ± .50	961.30 ± .56
2,3-Dimethyl-1-butene	C_6H_{12}	−14.78 ± .27	−27.713 ± .124	959.44 ± .28
3,3-Dimethyl-1-butene	C_6H_{12}	−14.25 ± .28	−30.103 ± .153	959.97 ± .29
2,3-Dimethyl-2-butene	C_6H_{12}	−15.91 ± .27	−26.576 ± .124	958.31 ± .28
1-Heptene	C_7H_{14}	−14.89 ± .44	−30.00 ± .40	1121.69 ± .45
1-Octene	C_8H_{16}	−19.82 ± .45	−30.00 ± .40	1279.13 ± .46
1-Nonene	C_9H_{18}	−24.74 ± .46	−30.00 ± .40	1436.58 ± .48
1-Decene	$C_{10}H_{20}$	−29.67 ± .48	−30.00 ± .40	1594.02 ± .50
1-Undecene	$C_{11}H_{22}$	−34.60 ± .50	−30.00 ± .40	1751.46 ± .52
1-Dodecene	$C_{12}H_{24}$	−39.52 ± .52	−30.00 ± .40	1908.91 ± .55
1-Tridecene	$C_{13}H_{26}$	−44.45 ± .56	−30.00 ± .40	2066.35 ± .59
1-Tetradecene	$C_{14}H_{28}$	−49.38 ± .59	−30.00 ± .40	2223.79 ± .62
1-Pentadecene	$C_{15}H_{30}$	−54.31 ± .62	−30.00 ± .40	2381.23 ± .66
1-Hexadecene	$C_{16}H_{32}$	−59.23 ± .66	−30.00 ± .40	2538.68 ± .70
1-Heptadecene	$C_{17}H_{34}$	−64.15 ± .70	−30.00 ± .40	2696.13 ± .74
1-Octadecene	$C_{18}H_{36}$	−69.08 ± .75	−30.00 ± .40	2853.57 ± .79
1-Nonadecene	$C_{19}H_{38}$	−74.00 ± .80	−30.00 ± .40	3011.01 ± .85
1-Eicosene	$C_{20}H_{40}$	−78.93 ± .84	−30.00 ± .40	3168.45 ± .89
Δ per CH_2; n>5	$-CH_2-$	−4.926	0.00 ± .40	157.443

[1] $\Delta Hf°_{298.16}$ represents the increment in the heat content or enthalpy of the process of forming the given hydrocarbon in the state indicated, from its elements, at 25° C, with all reactants and products in their appropriate standard reference states.

[2] $\Delta H\text{h}°_{298.16}$ represents the increment in heat content or enthalpy of the reaction of hydrogenation of the monoolefin to form the corresponding paraffin hydrocarbon, in the gaseous state at 25° C, with all reactants and products in their appropriate standard reference states.

[3] $\Delta Hc°_{298.16}$ represents the heat evolved in the combustion of the given hydrocarbon, in gaseous oxygen to form gaseous carbon dioxide and liquid water, at 25° C and constant pressure, with all reactants and products in their appropriate standard reference states.

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STUDIES OF BINARY AND TERNARY COMBINATIONS OF MAGNESIA, CALCIA, BARIA, BERYLLIA, ALUMINA, THORIA AND ZIRCONIA IN RELATION TO THEIR USE AS PORCELAINS

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ABSTRACT

Specimens formed by pressing were heated and tested for absorption and shrinkage to determine the vitrification range. These pressed specimens represented the various oxides in simple binary and ternary combinations and also with minor additions of auxiliary oxides. Vitrified pieces were tested for strength in compression, thermal conduction and expansion, electrical resistance, dielectric properties, water solubility, and resistance to attack by PbO liquid and vapor. Several compositions of unusual and valuable properties were disclosed. Phase relations were approximated by fusion tests and petrographic examinations of nonquenched samples.

CONTENTS

	Page
I. Introduction	277
II. Materials	279
III. Methods	280
IV. Results	284
1. The system BeO-Al_2O_3	284
2. The system MgO-BeO	287
3. The system MgO-Al_2O_3	289
4. The system MgO-BeO-Al_2O_3	289
(a) Fields of stability	292
(b) Ceramic bodies	293
(c) Reaction with water	296
5. The system CaO-BeO-Al_2O_3	297
6. The system BaO-BeO	297
7. The system BeO-Al_2O_3-ThO_2	297
(a) Fields of stability	299
(b) Ceramic bodies	299
8. The system BeO-Al_2O_3-ZrO_2	302
(a) Fields of stability	302
(b) Ceramic bodies	303
9. Resistance to attack by PbO	305
10. Effects of auxiliary oxides	305
(a) BeO–Al_2O_3–ThO_2 Series	308
(b) BeO–Al_2O_3–ZrO_2 Series	309
V. Summary	310
VI. References	312

I. INTRODUCTION

Conventional pottery bodies, which may be considered as including all types of ware from coarse earthen utensils to the most refined china or porcelain, are very complex and are composed of crystalline

silicates in a matrix or bond of glass. Since time immemorial these bodies have been dependent upon this bond of glass for the mechanical strength and dense structure necessary to their usefulness. This glass is essentially an alkaline, or alkaline earth, silicate usually derived from some form of feldspar in the raw batch. Like all glasses, it does not have a sharply defined fusion point but will soften, and deform under stress, at temperatures much lower than the temperature at which it becomes entirely liquid, and also much lower than the temperatures at which the crystalline phases of the body liquefy. The glass in addition, is likely to have other characteristics, such as thermal expansion, that differ from those of the crystalline phases.

If the pottery is intended for tableware, or even for cooking purposes in the relatively mild temperatures of a wood fire or a baking oven, the presence of a glass bond is no detriment to its utility. The presence of glass is detrimental, however, if the ware is subjected to stress at greatly elevated temperatures, or to thermal shock. Furthermore, the possibility of reducing mechanical strength because of internal stresses caused by differences in thermal dilation, or even by differences in shrinkage during the initial heating in the kiln, applies not only to a glass-crystalline system but also to a polyphase all-crystalline system. Theoretically, therefore, the desideratum is a monophase crystalline body, preferably of fine structure so as to avoid coarse intercrystalline surfaces that may be planes of weakness.

What may have been the earliest departure from the feldspathic compositions was the attempt by Hecht [1] [1] to produce a more nearly glass-free porcelain. In 1907 Bell [2] introduced free alumina into porcelain mixtures but retained a considerable percentage of feldspar. A further improvement in composition was the so-called Marquardt porcelain, made at the Royal Porcelain Factory in Berlin. In his reference to this porcelain, Howat [3] gave, as its composition, 35.12 percent of SiO_2, 63.20 percent of Al_2O_3, and 1.65 percent of K_2O. It is obvious that the composition was intended to produce a single-phase crystalline body because, at the time of World War I, it was thought that alumina and silica combined in artificial mixtures to form the silicate found in nature as sillimanite ($Al_2O_3.SiO_2$) containing 37 percent of SiO_2 and 63 percent of Al_2O_3. Consequently, investigators had as their object the production of porcelains with as high a percentage of sillimanite as it was practicable to obtain under industrial conditions.

Some years later [4] it was shown that sillimanite does not form in artificial preparations and that the ideal monophase aluminum silicate body is composed of mullite ($3Al_2O_3.2SiO_2$). Mullite contains 28.2 percent of SiO_2, 71.8 percent of Al_2O_3, and fuses at 1,810° C. Many porcelains manufactured today for exacting service conditions are essentially mullite, but contain interstitial glass resulting from reactions with fluxes added to make possible the vitrification of the body at manufacturing costs commensurate with the market value of the ware. Although the mullite body is giving good service in spark plugs, thermocouple protection tubes, chemical ware, and other articles for special uses, investigators have not relented in their search for other simple oxide combinations that can be used at temperatures exceeding even the fusion point of mullite.

[1] Numbers in brackets indicate the literature references at the end of this paper.

This search had been under way for some years as shown, for example, by English patents [5] covering the fabrication of articles from BeO, ThO_2, and ZrO_2. In Germany, interest in zirconia was very active as early as 1910 [6], and in this country the use of thoria crucibles for the refining of rhodium was described in 1929 [7]. The development of ceramic bodies of simple composition from pure oxides was not confined to the relatively rare oxides, and in 1929 German Patent No. 560,575 was granted for the making of articles from "aluminum oxide of high purity without special bonding agents." In 1924 the forming of shapes entirely from these nonplastic materials without the use of contaminating bonds was still beset with many difficulties according to Ruff [8] but, in 1935, Ryschkewitsch [9] stated that "the production of spark plug insulators of purest alumina, and single- or double-holed tubing of only a few tenths of a millimeter cross section of either beryllia or alumina, no longer presents a problem." The statement was too optimistic, but it did evidence an appreciable advance in the art. Many others have been active in this field during the past 15 years [10].

Under the impetus of the recent war, the generation and transmission of energy with greater and greater efficiency, and in ever-increasing quantities, is placing correspondingly greater demands upon engineering materials of all kinds, including ceramics. One illustration is the modern aviation engine, for which the spark plug of 20 years ago would be quite inadequate, and in which the practically single-phase alumina insulator is now used. Other developments, of which most are still on the restricted list of ordnance projects, either use ceramics that have been originated in recent years or have opened vistas of tremendous future possibilities for this type of material. In order to supply the fundamental information upon which the practical work of producing ceramics to meet these future possibilities can be based, there was undertaken a study of the characteristics of variously heated binary and ternary combinations of MgO, CaO, BaO, BeO, Al_2O_3, ThO_2, and ZrO_2, both as practically pure oxides and with minor additions of CaO, SrO, BaO, B_2O_3, SiO_2, TiO_2, or PbO. A preliminary report was published in 1941 [11], and the present paper reports results obtained since that time.

II. MATERIALS

In most cases the materials were the purest available commercially, but some oxides were especially prepared to further decrease contamination, as shown by the following descriptions. As prepared for use, the materials were in all cases at least sufficiently finely divided to pass the No. 325 U. S. Standard Sieve.

Alumina (Al_2O_3).—(1) Commercial grade usually used in making porcelain specimens and containing at least 99 percent of Al_2O_3 by analysis. Spectrograms showed medium strong lines for boron, weak lines for copper (probably abraded from the sieve), for sodium, and for silicon, and traces of several other elements.

(2) Laboratory prepared and usually used in bodies for fusion-point and softening-range determinations; obtained by dissolving aluminum of over 99.95-percent purity in nitric acid and igniting to the oxide. Spectrograms showed only very weak lines and traces of elements other than aluminum.

Barium oxide (BaO).—Introduced as reagent quality $BaCO_3$.

Beryllia (BeO).—(1) Commercial "SP grade," usually used in making the porcelain specimens, and nominally of 99.7-percent purity. Spectrograms showed only traces of copper, iron and magnesium, and very weak lines for silicon.

(2) Commercial "CP grade," usually used in specimens for fusion-point and softening-range determinations, nominally of over 99.9-percent purity.

Calcium oxide (CaO).—Introduced as reagent quality $CaCO_3$.

Magnesium oxide (MgO).—(1) Fused MgO (periclase) of approximately 97-percent purity, usually used in making porcelain specimens.

(2) Calcined $MgCO_3$ (calcining temperature given by producer as 2,000° F). Very fine grained, purity about 99 percent, and used in a relatively small number of specimens.

(3) Especially selected, water clear, crystals of periclase,[2] which were hand ground in agate or mullite mortars and usually used in bodies for fusion-point and softening-range tests. The purity is nominally over 99 percent.

Silica (SiO_2).—Pulverized natural quartz of 99.6-percent purity.

Strontia (SrO).—Introduced as reagent quality $SrCO_3$.

Titania (TiO_2).—Trade designation "pigment grade," purity about 99 percent, with Fe_2O_3 given by the producer as less than 0.2 percent.

Thoria (ThO_2).—Calcined thoria, nominally of over 99-percent purity. Spectrograms showed only very weak lines for calcium, copper, and silicon, and no other impurities were indicated.

Zirconia (ZrO_2).—A CP grade of calcined zirconia, and recalcined at 1,440° C. The spectrogram showed medium lines for columbium and titanium and only very weak lines or traces for calcium, copper, iron, magnesium, lead, and silicon.

In order to obtain the desired fineness of particle size, it was necessary to grind the SP BeO, the commercial grade Al_2O_3, and the ThO_2. The BeO described above had been ground wet for 2 hours in porcelain-lined mills with flint pebbles. The Al_2O_3 and the ThO_2 had been ground for 48 hr. in a steel mill with steel rods, and then purified by treatment with diluted HCl until the wash water gave a negative test for iron.[3]

III. METHODS

Specimens were prepared during the first stages of the work by hand-mixing the ingredients in slip form, drying, pulverizing in an agate or in a mullite mortar, remixing with a 5-percent solution of soluble starch, and pressing in hardened steel moulds. About 14 g of the starch solution was used for 100 g of dry batch, and the forming pressure was 9,300 lb/in^2. Later, the method was improved by machine-blunging the slip with a chemical-laboratory-type stirrer, and by vibrating the dampened mixture in the steel moulds before pressing. The pressed specimens were matured in an electric furnace, heated with eight ThO_2-Y_2O_3 resistors, described in Bureau Research Paper RP1662 [12]. The heating and cooling rates were maintained very close to 3°C per min, and the holding time at the maximum temperature usually was 1 hr. A typical setup with three specimens

[2] Furnished by the Vitrefrax Corporation and by the Norton Co.

[3] Comparative tests were made also on specimens of mixtures containing ThO_2 that had been fused in an electric arc, ground in the steel mill, and acid-treated, but the results reported are for bodies made with the calcined thoria only.

for the crushing test is shown in fig. 1, *A*. All temperature measurements in the maturing treatment, and also in the softening-range and melting-point tests, were made with a Leeds & Northrup optical pyrometer calibrated at the Bureau.

For the softening-range and fusion tests, small four-sided pyramids about $\frac{1}{16}$ in. at the base and grooved on each side, as shown in figure 1, *B*, were ground from pressed, unfired pieces and were tested in the furnace described in Bureau Research Paper RP1443 [11].

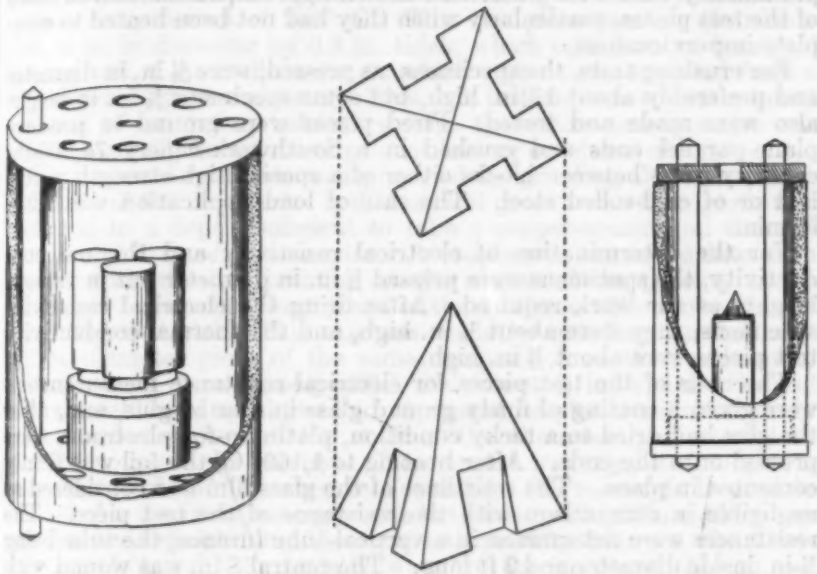

FIGURE 1.—*Furnace arrangements for heating specimens.*

A, Setup for heating three specimens to vitrification. Specimens measure about 0.55 in. in diameter by 1.1 in. long, and rest on platinum-rhodium disks. They are shown in the heating chamber of an eight-resistor furnace, described in J. Research NBS **35** 87 (1945) RP1662.
B, Shape of specimen for fusion tests. These were ground from pressed blanks and measure about $\frac{3}{16}$ in. square at the base.
C, Specimen for fusion test, shown in the three-resistor furnace described in J. Research NBS **27** 555 (1941) RP1443. The specimen rests on a rhodium plate supported by a ThO_2, ZrO_2, or BeO pedestal.

The furnace arrangement for softening-range and fusion tests is shown in figure 1, *C*. The specimen rests upon a disk of rhodium, or of 20 percent rhodium–80 percent platinum, depending upon the maximum temperature to be reached, and the metal disk in turn is supported on a pedestal of ZrO_2, ThO_2, or BeO. By careful placement of the disk so that its flat (or slightly concave) upper surface is perpendicular to the line of vision, an effect is obtained in which the metal surface reflects less light to the pyrometer than the specimen does. As a result, the metal appears slightly colder than the specimen and makes it visible in outline. For a typical specimen, this outline will appear as shown at the top in figure 1, *B*, except that the diagonals representing the edges from base to apex would not be visible. The temperature rise as the fusing temperature was approached, and during fusion, was held as close as possible to a rate of from 1° C to 2° C per min.

Shrinkage values were based on micrometer measurements of the diameter of specimens when dry, and after having been fired. Absorption values were obtained by boiling the fired specimens in carbon tetrachloride for 5 hr, permitting them to cool in the liquid until the next day, and determining the increase in weight. The weight increase was divided by the density of the CCl_4 in order to make the values comparable with data obtained conventionally by boiling the specimens in water. CCl_4 was used as the saturating medium because preliminary tests with water had shown appreciable solution of some of the test pieces, particularly when they had not been heated to complete imperviousness.

For crushing tests, the specimens, as pressed, were ⅝ in. in diameter and preferably about 1¼ in. high, but some specimens ⅝ in. in height also were made and tested. Fired pieces were ground to produce plane-parallel ends and crushed in a Southwark-Emery 75,000-lb-capacity press between blocks either of a special high-strength porcelain or of cold-rolled steel. The rate of load application was 6,250 lb/min.

For the determination of electrical resistivity and thermal conductivity, the specimens were pressed ⅝ in. in diameter but in various heights as the work required. After firing the electrical resistivity specimens, they were about ⅛ in. high, and the thermal-conductivity test pieces were about ¼ in. high.

The ends of the test pieces for electrical-resistance measurements were given a coating of finely ground glass in diluted glue, and, after the glue had dried to a tacky condition, platinum-foil electrodes were pressed onto the ends. After heating to 1,100° C, the foil was firmly cemented in place. The resistance of the glass film was considered as negligible in comparison with the resistance of the test piece. The resistances were determined in a vertical-tube furnace, the tube being ⅞-in. inside diameter and 2 ft long. The central 8 in. was wound with 80-percent-Pt–20-percent-Rh wire, and the temperature was controlled with a Wheatstone bridge-type regulator [13]. This regulator maintained an average temperature to ± 0.1 deg C, and the variation over the test piece, during the 10 min that a specimen was held at a given temperature before a resistance measurement was made, did not exceed ± 1.5 deg C.

In the furnace, the test specimen was held at the center of the hottest section between platinum electrodes affixed to the ends of mullite tubes, through which the thermocouple and connecting wires were placed. These tubes were concentrically located in the furnace tube by means of alumina guide disks. Resistances were measured on a Weston ohmmeter, model 764, and a 60-cycle current of a few microamperes was put through the test piece, thus avoiding polarization and also any appreciable heating effects from the measuring current. The lead wires from the instrument to the furnace were kept well separated to minimize capacitance-conductance effects. This method was devised by E. N. Bunting.

The resistance was assumed to be largely volume resistance, for which the specific value may be expressed as $\rho = RA/L$, where R is the measured resistance in ohms, A is the area of the end of the specimen in square centimeters, and L is the average thickness of the specimen in centimeters. Resistance measurements were usually made at 25 deg C intervals. By plotting log ρ against temperature,

an approximately straight line was obtained, represented by the equation $\rho=c-bt$, where c and b are constants, and t is in degrees centigrade. The T_e value, which is the temperature at which ρ equals 1 megohm, could then be obtained by interpolation from this line.

The thermal-conductivity values are purely relative, and are expressed as 100 times the reciprocal of the temperature drop in degrees centigrade across a one-half-inch height of specimen approximately one-half inch in diameter when resting on a hot plate with a surface temperature of 250° C. This hot plate was an aluminum disk, 8 in. in diameter by 0.5 in. thick, which rested on an insulated heating coil, 4 in. in diameter, to which current was supplied from a constant-voltage transformer. This coil, in turn, was supported on a pedestal of insulating refractory, and the entire arrangement was located centrally in a cubical cabinet having a volume of 8 ft^3.

The matured specimen was prepared by grinding the ends plane-parallel and 0.5 in. apart. A diametrical groove was then ground in each end to a depth sufficient to take a copper-constantan thermocouple of 0.01-in.-diameter wire. A couple was cemented into each groove, with the hot junction at the center of the groove, and a "cap" was fastened to the top end of the specimen with a minimum of cementing material. This cap was made by grinding another one-half-in.-diameter piece of the same composition as the specimen so that the ends were plane-parallel and about ¼ in. apart. Several such assemblies of specimen and cap could be placed simultaneously upon the hot plate and the ends of the thermocouples carried to junctions outside the cabinet. The current was regulated to give a temperature of 250° C when read with the thermocouple located in the end of a specimen resting on the hot plate. When the entire setup had reached equilibrium, the temperature drop between the "hot-plate couple", and the couple between the specimen and the cap was recorded for each specimen assembly.

Determinations of relative resistance to the attack of PbO[4] were made in two ways, using specimens which had been pressed ⅝ in. in diameter and ½ to ¾ in. high. In one, the PbO was placed in a 25-ml platinum crucible and covered with a regular platinum crucible cover through which several large holes had been drilled. The weighed specimen, supported by a small tripod of BeO, was placed on the lid and covered with an inverted 25-ml platinum crucible. The entire assembly was placed within an electric furnace, using 80-percent Pt-20-percent Rh as the resistance element, and heated for 4 hr, usually at 1,100° C. After this treatment, the specimen, together with a comparable untreated piece or "blank" of the same composition, was immersed in a 1-to-1 solution of HNO_3 on a hot plate for about 16 hr, washed, redried at 500° C, and weighed. In the other method, the lid between the two crucibles was omitted and the specimen placed directly in the molten PbO. Because the specimens floated on the molten PbO and were only partly immersed, numerical values are not comparable, and resistance to solution was judged by inspection.

[4] These determinations were designed to measure the relative resistance to attack of a porcelain in vapors containing lead oxide. Such vapors are found in the cylinders of internal-combustion engines using a fuel with an admixture of tetraethel lead.

For the thermal-expansion tests, using the interferometer method [14], disks about 5/16 in. high and 1 in. in diameter were first matured and then ground to the shape of a V with raised portions, or feet, on both sides at the apex and at the end of each leg.

Specimens for the determination of dielectric constant and power factor were pressed 1¼ in. in diameter and about 5/16 in. in height. The tests were made by C. M. Sparks and Arnold H. Scott in the Inductance and Capacitance Section of the Bureau, using the bridge and the method described in Bureau Research Paper RP1457 [14a].

The fact that many of the temperatures involved in the phase studies were above the melting point of platinum would greatly increase the mechanical difficulties of efficiently quenching the specimens. For the phase studies reported here, the preparations examined were obtained mostly from fusion determinations. Their firing time was comparatively short; many were not fused completely to liquid, and none was quenched. Therefore, it is apparent that equilibrium was obtained only rarely, and the equilibrium conditions at elevated temperatures were not established. With this in mind, the proposed phase relations were based primarily on fusion behavior. The fusion behavior of the compositions, combined with petrographic and X-ray examinations, is, however, believed to be strongly indicative of the true equilibrium conditions.

IV. RESULTS

1. THE SYSTEM BeO-Al_2O_3

A paper by Wartenburg and Reusch [15] on the system BeO-Al_2O_3 reports a simple eutectic at 80 wt percent of Al_2O_3 and 1,890° C, with no indication of a compound. Their determinations involved rapid fusion to a bead in an oxypetroleum flame and also rapid cooling. In the present investigation the compound $BeO.Al_2O_3$, corresponding to the mineral chrysoberyl, was obtained readily either by sintering or by fusing the intimately mixed oxides. The results indicate also a eutectic at about 1,880° C and 14 wt percent of BeO and at about 1,865° C and 27 wt percent of BeO, as shown by the following data.

A mixture in equimolar ratio of SP BeO and the commercial Al_2O_3 (19.7 and 80.3 wt percent, respectively) fused at 1,880° C and crystallized in laths, some of which were as large as 1 by 3 mm. These laths were chrysoberyl and had the following optical properties: biaxial +; optic angle about 45°; indices of refraction—alpha 1.747, beta 1.748, gamma 1.756. A similar mixture, using CP beryllia and the laboratory-prepared alumina, fused at 1,890° C and crystallized as long, clear prisms of chrysoberyl with properties as given for the crystals in the less pure mixture. With the same pure oxides, the mole composition $BeO:4Al_2O_3$ (5.78 wt percent of BeO) fused at 1,920° to 1,925° C; $BeO:2Al_2O_3$ (10.9 wt percent of BeO) fused between 1,885° and 1,900° C; $2BeO:3Al_2O_3$ (14.06 wt percent of BeO) fused at 1,880° to 1,885° C; $1.5BeO:Al_2O_3$ (26.91 wt percent of BeO) fused sharply at 1,865° C; $2BeO:Al_2O_3$ (32.9 wt percent of BeO) began to fuse at 1,875° C, but fusion was far from complete at 1,880° C; and $4BeO:Al_2O_3$ (49.5 wt percent of BeO) showed no fusion at 1,915° C.

The fusion behavior of the compositions between the chrysoberyl-beryllia eutectic and beryllia indicates solid solution. X-ray powder

TABLE 1.—*Values for physical and dielectric properties of binary compositions and component oxides*

Specimen from test No.	Composition						Matured at—	Number of specimens	Physical properties				Number of specimens	Absorption	Dielectric properties at 100 kc/s[a]	
	Mole			Weight					Absorption	Linear shrinkage	Bulk density	Compressive strength[b]			Constant	Loss angle
	MgO	BeO	Al_2O_3	Calcined MgO	SP BeO	Al_2O_3[c]										
				%	%	%	°C		%	%		lb/in.²		%	K	tan δ
106-L	0	0	1	0	0	100	1,875	2	0.18	11	3.69	71,000	2	0.11	9.1	0.0020
107-L	0	0	1	0	0	100	1,905	3	.18	11	3.73	62,000				
110-L	0	0	1	0	0	[d]100	1,835	3	.18	11	3.73	156,000				
99-L	0	0	1	0	0	[e]100	1,930						2	.14	8.7	.0003
127-L	0	1	1	0	19.7	80.3	1,840	3	.01	9	3.23	119,000				
155-L	0	1	1	0	19.7	[e]80.3	1,840	3	.01	[f]17	3.26	109,000				
89-L	0	1	1	0	19.7	80.3	1,860	3	.04	9	3.27	119,000				
121-L	0	1	1	0	19.7	80.3	1,865						3	.00	[g]7.7	[g].0001
101-L	0	1	0	0	100.0	0	1,925	3	.03	18	2.79	128,000	2	.14	6.3	.0024
96-L			1	1	99.0	0	1,850	3	.01	18	2.85	117,000	2	.01	6.5	.0007
128-L	1	10	0	13.8	86.2	0	1,830	1	.01	21	2.91	157,000				
153-L	1	10	0	13.8	86.2	0	1,600	3	.02	22	2.86	94,000				
117-L	1	0	1	28.3	0	71.7	1,950	3	.26	6	3.15	99,000	3	.02	7.2	.0037

[a] Commercial Al_2O_3, except as noted.
[b] The compression tests were made with the nominal 0.5-in.-diameter by 1-in.-long specimens between contact blocks of special high-temperature porcelain (see table 2).
[c] The dielectric values were determined by C. M. Sparks and A. H. Scott.
[d] Decanted "fines" from commercial Al_2O_3.
[e] Laboratory-prepared Al_2O_3 of 99.95-percent purity.
[f] This comparatively high shrinkage is accounted for by the fact that the Al_2O_3 used in the mixture was the calcined laboratory-prepared material of 99.95-percent purity.
[g] Fired-on silver electrodes.

patterns do not support this, but they do support the assumption that no other compound of BeO and Al_2O_3 is formed. Petrographic and X-ray examinations also revealed that only one phase ($BeAl_2O_4$) was present in samples of $2BeO:3Al_2O_3$, $BeO:2Al_2O_3$, and $BeO:3Al_2O_3$. The absence of alumina in these specimens indicates that solid solution had occurred. In the composition $BeO:4Al_2O_3$, inclusions of alumina were present as rounded grains of corundum. The crystallographic evidence is, therefore, that chrysoberyl can take at least 2 moles, but not 3 moles, of alumina into solid solution.

Three tests on two vitreous pieces of $BeAl_2O_4$ produced T_s values ranging from 1,270° to 1,285° C, and six observations of thermal conductivity on one of these pieces gave an average value of 3.4. Specimens for the determination of absorption, shrinkage, strength in compression, and dielectric properties were heated at 1,840° to 1,865° C (table 1). Chrysoberyl specimens of uniformly fine crystal texture were not obtained. Even 1,840° C, the minimum temperature for complete vitrification,[5] produced also an undesirably coarse crystal texture. For example, one of several rods of $BeAl_2O_4$, heated at 1,840° C for 1 hr, contained crystals ranging in size from 20 to 3,000 microns (fig. 2). This particular specimen had an absorption of less than 0.01 percent and failed in the crushing test at 114,000 lb/in^2. Average values for nine similar specimens are given in table 1.

The crushing tests were made with the specimen between porcelain blocks. Experiments made later in the investigation, and recorded in table 2, proved that the maximum compressive strength was not developed with the porcelain blocks and that more consistent, and significantly higher, values can be obtained with cold-rolled-steel blocks. The two porcelains referred to in table 2 are commercial compositions, and the test pieces were made under very carefully controlled industrial conditions. Preliminary tests demonstrated also that steel blocks ¼-in. in thickness were not suitable (fig. 3), and the reported values were obtained with blocks three-quarter-inch thick. In addition to showing the advantage of using steel blocks, the values given in table 2 show that higher values were obtained for specimens with a length to diameter ratio of about 2:1, as compared to those with a ratio of about 1:1, and for glazed as compared to unglazed specimens.

The following values were obtained for the average coefficients of linear thermal expansion of chrysoberyl (multiply the values by 10^{-6}): Room temperature to 100° C, 5.6; 100° to 200° C, 7.1; 200° to 300° C, 7.8; 300° to 400° C, 8.7; 400° to 500° C, 9.6; 500° to 600° C, 9.8; 600° to 700° C, 9.7; 700° to 800° C, 9.8; 800° to 900° C, 8.8; and 900° to 1,000° C, 9.2. The percentage expansion from room temperature to 1,000° C was 0.788.

A limited number of tests were made on specimens composed entirely of BeO or of Al_2O_3 (table 1). Very small percentages of impurities have a pronounced effect on the vitrification behavior of beryllia. The SP grade could be vitrified at 1,800° C, but the CP grade showed an absorption of 20 percent at 1,800° and 6.1 percent at 1,900° C. Some photomicrographs of typical crystal growths for both types of Al_2O_3 are shown in figures 4 and 5, and representative values for strength in compression, and for dielectric constant and loss angle, are given in table 1. The T_s value for three vitreous specimens of

[5] In this investigation, a completely vitrified structure is defined arbitrarily as one having an absorption of less than 0.1 percent.

FIGURE 2.—*Photomicrograph, taken with crossed polarized light, showing crystal development in a specimen of chrysoberyl* ($BeAl_2O_4$) *heated at 1,840° C.*

The distance between the arrow points at the left represents a length of 1 mm.

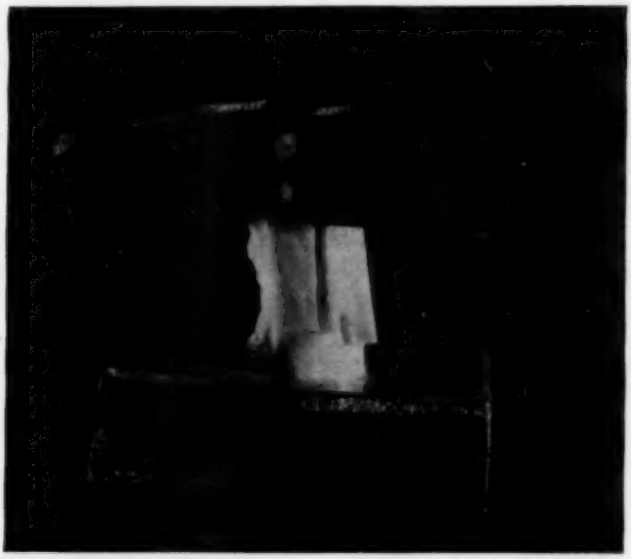

FIGURE 3.—*Penetration and rupture of a ½ in. thick cold-rolled steel block by a ½-in. diameter specimen of a commercial porcelain during test in compression. The porcelain failed at 332,000 lb/in².*

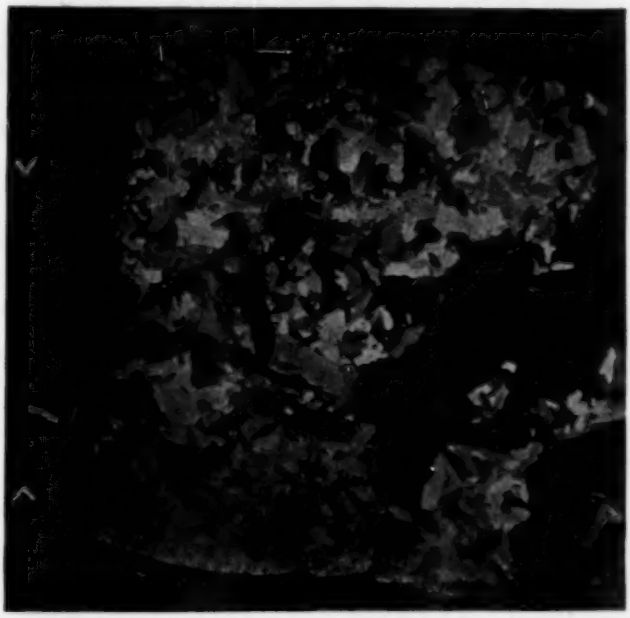

FIGURE 4.—*Photomicrograph, taken with crossed polarized light, showing crystal development in a specimen of commercial alumina heated at 1,905°C.*

The distance between the arrow points at the left represents a length of 1 cm.

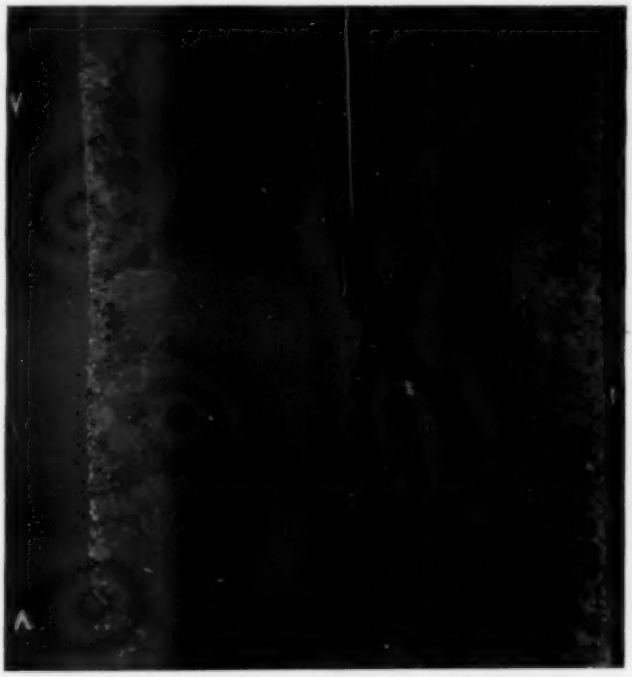

FIGURE 5.—*Photomicrograph, taken with crossed polarized light, showing crystal development in a specimen of laboratory-prepared alumina (99.95 percent Al_2O_3) heated at 1,890°.*

This is a longitudinal section of a rod. At the original outer surface, and to a depth of about 0.7 mm, the crystals average 30 microns in size. The next concentric layer, about 1.5 mm wide, contains crystals averaging 400 microns in size. The center portion is very fine grained, the crystals averaging about 5 microns in size.

The distance between the arrow points at the left represents a length of 1 cm.

commercial alumina ranged from 1,076° to 1,167° C. For two specimens of the laboratory-prepared alumina the values were 1,102° and 1,186° C, and for an artificial single crystal,[6] the value was 1,214° C parallel to, and 1,231° C, perpendicular to, the *c* axis. For one specimen of BeO (table 3) the value was 1,177° C, for another it was 1,230° C. Nine observations of relative thermal conductivity on two alumina specimens gave the average value 3.6, and for two beryllia specimens (table 3) the value was 12.5.

TABLE 2.—*Effect of contact blocks, glazing, and length-diameter ratio of specimens on resistance to crushing*

Nominal length	Average length-diameter ratio	Number of specimens	Glazed	Contact blocks	Compressive strength
			Porcelain No. 3		
In.					*lb./in.*[2]
1	2.13	5	Yes	Cold-rolled steel	316,000±12,000
½	1.15	11	do	do	271,000±8,000
1	2.15	5	do	Porcelain	231,000±24,000
1	2.18	5	No	do	205,000±26,000
1	2.13	5	Yes	Cold-rolled steel	316,000±12,000
1	2.20	4	No	do	208,000±24,000
1	2.15	5	Yes	Porcelain	231,000±24,000
1	2.13	5	do	Cold-rolled steel	316,000±12,000
1	2.18	5	No	Porcelain	205,000±26,000
1	2.20	4	do	Cold-rolled steel	208,000±24,000
			Porcelain No. 4		
1	2.06	4	Yes	Porcelain	215,000±25,000
½	1.01	6	do	do	170,000±12,000
1	2.01	4	do	Cold-rolled steel	303,000± 3,000
½	1.03	8	do	do	262,000±10,000
1	2.01	4	do	do	303,000± 3,000
1	2.10	12	No	do	262,000±10,000
1	2.06	4	Yes	Porcelain	215,000±25,000
1	2.01	4	do	Cold-rolled steel	303,000± 3,000
½	1.01	6	do	Porcelain	170,000±12,000
½	1.03	8	do	Cold-rolled steel	262,000±10,000

2. THE SYSTEM MgO-BeO

In 1937, Wartenburg and coworkers [16] reported a simple eutectic at 1,860° C and 50 wt percent of BeO. This is in good agreement with the results of the present investigation, in which the mixture containing 48.2 wt percent of BeO (MgO:1.5BeO mole ratio) fused sharply at 1,855° C. In comparison, mixtures with 38.3 wt percent (MgO:BeO mole ratio), 55.4 wt percent (MgO:2BeO mole ratio), and 65.1 wt percent of BeO (MgO:3BeO mole ratio) were not completely fused after holding at 1,875° C. The following petrographic report contains no evidence of solid solution or of compound formation in this system, and is in accord with the indication of the fusion tests that the mole composition MgO:1.5BeO is at, or very near, the eutectic:

MgO:BeO (*heated at 1,860° C*).—The texture was characteristically in a radial, or fan shaped, arrangements of crystals resulting from the co-crystallization of thin plates of MgO and BeO. The core of these

[2] Furnished by the Linde Air Products Co.

fan shapes is composed of MgO. This composition is definitely on the MgO side of the eutectic, as shown by the presence of free magnesia grains.

MgO:1.5BeO (*heated at 1,855° C*).—The core of the fan-shaped formations is composed of BeO and of MgO crystals as polygonal sintered grains. The outer portions consist mainly of BeO and MgO in intergrowth texture. This composition appears to be at, or near, the eutectic.

MgO:2BeO (*heated at 1,875°*).—Crystals at the edge of the specimen show an unusual texture made up of irregular plates of BeO and MgO in alternate positions. The core of the fan-shaped crystal growths is predominantly BeO.

MgO:3BeO (*heated at 1,875°*).—The crystals are rounded in appearance and have a botryoidal structure. They are composed of BeO and MgO in intergrowth texture. Judging from the relative amounts of this texture, this specimen is further from the eutectic than is MgO:2BeO.

Compositions containing not more than about 21.2 wt percent of MgO (mole ratio MgO:6BeO) could be vitrified. The temperature range over which vitrification was attained decreased with increase in MgO content, and all the vitrified bodies had a relatively coarse crystal texture, the tendency being for the coarseness to increase with increase in percentage of MgO and with increase in the temperature of heating. Composition MgO:10BeO was typical and consisted of MgO in a fine mosaic, with BeO in rounded and irregular grains averaging about 15 microns in size, when heated at 1,560° C. When heated at 1,850° C, the MgO was present in small grains with cubic cleavage, and the BeO crystals had grown as large as 70 microns in maximum dimension. Four specimens were tested for strength in compression (see tests 128–L and 153–L, table 1), and values for electrical resistance and thermal conductivity are given in table 3.

TABLE 3.—*Absorption, linear shrinkage, electrical resistivity, and thermal conductivity values for* BeO, *for* MgO, *and for mixtures of these oxides*

Specimen from test No.	Composition				Matured at—	Absorption	Shrinkage	Electrical resistivity [a] (T_e value)	Thermal conductivity [b]
	Mole		Weight						
	MgO	BeO	MgO	BeO					
			%	%	°C	%	%	°C	
81–L				100	1,880	0.09		1,177	12.5
98–L				100	1,925	.03	19.0	1,230	12.5
39–L			1	99	1,875	.18	19.0	1,210	
171			1	99	1,930	.01	20.0	1,191	12.5
33–L			2	98	1,875	.07	23.0	1,029	
189			5	95	1,835	.03	17.6	1,200	12.5
140	1	15	9.7	90.3	1,855	[c]1.43	20.0	1,190	
236	1	15	9.7	90.3	1,830	0.00	20.0	1,206	
235	1	10	13.9	86.1	1,830	.01	20.6	1,169	12.5
234	1	4	28.7	71.3	1,835	.23	23.1	1,186	12.5
211	1	3	34.9	65.1	1,835	.37	16.8	1,150	7.1
214	1	2	44.6	55.4	1,835	.43	16.3	1,201	6.2
[d]			100					1,232	2.5

[a] The T_e value for electrical resistivity is the temperature at which, by calculation based on test values, a 1-cm cube of the material has a resistance of 1 megohm. The values were obtained by E. N. Bunting.
[b] These values are the reciprocal, multiplied by 100, of the temperature drop through a 0.5-in. height of specimen approximately ½ in. in diameter. The values were determined by E. N. Bunting.
[c] This value was obtained by boiling the specimen in water, causing partial hydrolysis.
[d] Specimen cut from a single crystal of periclase.

3. THE SYSTEM MgO-Al_2O_3

The system has been explored by Rankin and Merwin [17], and no work was done on it in this investigation beyond a limited number of tests on the compound $MgAl_2O_4$ (spinel). For some results, see test 117–L, table 1. In addition, a specimen heated at 1,900° C, and having an absorption of 0.10 percent, gave a thermal-conductivity value of 1.9, and for a section of this specimen, the T_e value was 1,170° C. It was noted also that when equimolar mixtures of MgO and Al_2O_3 were heated for 15 min at 1,700° C and at 1,800° C, the conversion to spinel was over 95 percent complete. Heating the mixture for the same length of time at 1,650° C caused 80- to 90-percent conversion. The following average coefficients of linear thermal expansion were obtained for a spinel sample that had been fired at 1,800° C (multiply values by 10^{-6}): room temperature to 100° C, 6.0; 100° to 200° C, 7.5; 200° to 300° C, 8.1; 300° to 400° C, 8.7; 400° to 500° C, 9.0; 500° to 600° C, 9.0; 600° to 700° C, 8.9; 700° to 800° C, 8.6; 800° to 900° C, 7.4; 900° to 1,000° C, 7.1. The specimen had reacted with the fused-silica interferometer plates, which may explain the decreasing coefficients for the temperature intervals above 600° C.

4. THE SYSTEM MgO-BeO-Al_2O_3

The only information found in the literature on this system is contained in patents [18]. The phase relations indicated by the fusion behavior of the 41 compositions examined in the present study are shown in figure 6. According to these indications, the greater por-

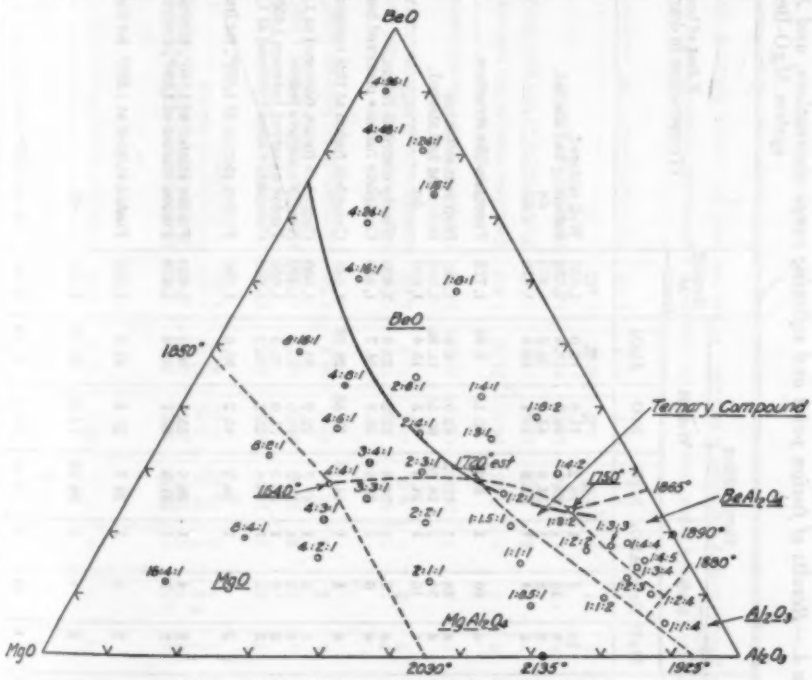

FIGURE 6.—*The system* MgO–BeO–Al_2O_3.

Compositions between the BeO apex and the heavy solid line could be heated to a non-porous structure (i. e., vitrified) over a temperature range of at least 25 deg C.

TABLE 4.—*Results of fusion point and softening range observations, and X-ray and microscopical examinations of the tested specimens in the system* MgO-BeO-Al_2O_3

Test No.	Composition: Mole MgO	Mole BeO	Mole Al_2O_3	Weight MgO	Weight BeO	Weight Al_2O_3	Heated at (max)—	Effect of heating (Temperatures in degrees centigrade)	Results of X-ray and microscopical examinations (Specimens examined were not quenched and the phases observed may not be those in equilibrium at the maximum temperature of heating or at the liquids)
				%	%	%	°C		
122	16	4	1	76.2	11.8	12.0	1,650	Well sintered.	
66–L	8	16	1	39.1	48.5	12.4	1,670	Softening had started.	
64–L	8	8	1	34.8	43.2	22.0	1,670	do	
226	8	4	1	61.5	19.1	19.4	1,670	do	Crystalline phases: periclase, bromellite and spinel. Mosaic texture. Average grain size 20 to 25 microns.
148	4	96	1	6.05	90.15	3.80	1,775	Porcelain-like structure	Bromellite, with rare grains of periclase and spinel. Grain size of bromellite 25 to 85 microns.
151	4	48	1	11.02	82.02	6.96	1,685	Incipient softening.	
151	4	24	1	18.65	69.55	11.80	1,685	Softening had started.	
111	4	16	1	24.3	60.3	15.4	1,650	do	X-ray pattern contains only lines for periclase, bromellite, and spinel.
63–L	4	8	1	34.8	43.2	22.0	1,670	Nearly complete fusion.	
194	4	6	1	39.0	36.3	24.7	1,655	Complete fusion observed between 1,650° and 1,655°.	
351	4	4	1	44.40	27.55	28.05	1,640	Complete fusion at this temperature	X-ray pattern of specimen heated at 1,710° C gave only lines for periclase, bromellite, and spinel.
70–L	4	3	1	47.7	22.2	30.1	1,660	Complete fusion (sintered at 1,650°).	
63–L	4	2	1	51.5	16.0	32.5	1,670	Nearly complete fusion.	
426	3	4	1	37.5	31.0	31.5	1,655	Fusion observed between 1,650° and 1,655°.	
70–L	3	3	1	40.6	25.2	34.2	1,660	Complete fusion (sintered at 1,650°).	
423	2	6	1	24.2	45.2	30.6	1,680	Fusion started at 1,650°, far from complete at 1,680°	A specimen heated at 1,750° contained bromellite, and BeO with spinel in graphic intergrowths, indicating BeO as the primary phase.
419	2	4	1	28.5	35.5	36.0	1,660	Fusion started at 1,640°, incomplete at 1,660°	Do.
425	2	3	1	31.3	29.1	39.6	1,670	Fusion started at 1,650°, incomplete at 1,670°	A specimen heated at 1,660° C showed a "grating" texture interstitial to BeO crystals, indicating proximity to a field boundary.
408	2	2	1	34.7	21.5	43.8	1,700	Fusion started at 1,675°, far from complete at 1,700°	Crystals of BeO, spinel, and MgO in complete graphic form, indicating proximity to a field boundary. The specimen examined had been fused at 1,750° C.
407	2	1	1	38.85	12.05	49.10	1,700	do	Well-developed crystals of BeO and spinel in graphic intergrowth texture. Occasional irregular grains of MgO. Textural appearance indicates spinel as the primary phase.
149	1	24	1	5.45	80.80	13.75	1,740	Porcelain-like structure	Bromellite is the only crystal phase identified. Average range in grain size is 20 to 40 microns.
57–L	1	16	1	7.42	73.80	18.78	1,805	Softening had started.	
55–L	1	8	1	11.80	58.45	29.75	1,778	Complete fusion (started at 1,755°)	Bromellite, both in blocky grains and as intergrowths with spinel.
199	1	4	1	16.6	41.3	42.1	1,755	Complete fusion observed between 1,750° and 1,755°.	
197	1	3	1	18.55	34.55	46.90	1,750	Complete fusion observed between 1,745° and 1,750°	Well-developed crystals of bromellite and spinel in graphic

145	1	24	1	8.45	80.80	13.75	1,740	Porcelain-like structure	Bromellite is the only crystal phase identified. Average range in grain size is 20 to 40 microns.
57-L	1	16	1	7.42	73.80	18.78	1,805	Softening had started.	
55-L	1	8	1	11.80	58.45	29.75	1,775	Complete fusion (started at 1,755°)	Bromellite, both in blocky grains and as intergrowths with spinel.
199	1	4	1	16.6	41.3	42.1	1,755	Complete fusion observed between 1,750° and 1,755°.	
197	1	3	1	18.55	34.55	46.90	1,750	Complete fusion observed between 1,745° and 1,750°	Well-developed crystals of bromellite and spinel in graphic texture.
198	1	2	1	21.0	26.0	53.0	1,760	Complete fusion between 1,755° and 1,760°	BeO in parallel orientation with spinel, possibly an unmixing texture. X-ray shows only lines for bromellite and spinel. For a specimen heated at 1,740°, both X-ray and petrographic examination showed the presence, in small percentage, of the "ternary" phase.[b]
422	1	1.5	1	22.45	20.90	56.65	1,745	Complete fusion observed between 1,740° and 1,745°	Crystals of bromellite and spinel in graphic texture.
55-L	1	1	1	24.10	14.96	60.94	1,775	Fusion nearly complete (started at 1,730°)	Do.
49-L	1	0.5	1	26.03	8.08	65.89	1,800	Softening had started	Spinel containing some bromellite in lath formation.
112-L	1	6	2	10.22	38.05	51.73	1,765	Well sintered	Spinel, BeO, and a third phase which could not be identified, but may be the "ternary" compound.
109-L	1	4	2	11.7	29.1	59.2	1,760	Fusion nearly complete	Principal phase may be ternary compound. Spinel and BeO also present.
421	1	3	2	12.65	23.50	63.85	1,750	Complete fusion between 1,748° and 1,750°	Principal phase may be ternary compound. Chrysoberyl ($BeAl_2O_4$) and BeO also present.
355	1	2	2	13.7	17.0	69.3	1,790	Complete fusion between 1,765° and 1,770°	About 60 percent is the possible ternary phase. Remainder, BeO, with rare grains of spinel. When heated at 1,850°, or fused in an oxyflame, product was over 98 percent large crystals of the "ternary" phase.
352	1	1	2	14.95	9.30	75.75	1,880	Fusion started at 1,830° and not complete at 1,880°	Apparently all one phase.[b]
119-L	1	3	3	9.6	17.8	72.6	1,750	Complete fusion observed between 1,755° and 1,760°	Crystals mostly the "ternary" compound, BeO intergrown with the "ternary" compound, and small amounts of chrysoberyl and spinel.
118-L	1	2	3	10.15	12.65	77.20	1,780	Complete fusion observed between 1,765° and 1,775°	Principal phase is spinel with the "ternary" phase second in quantity, and BeO rare.
47-L	1	4	4	7.35	15.25	74.40	1,800	Complete fusion at this temperature	Principal phase is chrysoberyl, with spinel and the "ternary" phase in small amounts.
240	1	3	4	7.70	14.35	77.95	1,810	Fused sharply at this temperature	Chrysoberyl 85 percent, spinel 10 percent, and rare grains of the "ternary" phase.
118-L	1	2	4	8.15	10.12	81.73	1,770	Softening had started	Corundum 15 percent, spinel 10 percent, remainder very fine-grained birefringent crystals.
50-L	1	1	4	8.5	5.3	86.2	1,855	----do	Spinel, corundum, and chrysoberyl in about equal quantities.
48-L	1	4	5	6.2	15.4	78.4	1,835	Fusion started at 1,790°, complete at 1,835°	Principal phases are chrysoberyl and the "ternary" compound, with spinel rare.

[a] The term "complete fusion" means that the pyramidal specimen had fused sufficiently to flow into a flat button shape, and does not necessarily connote that the mixture had completely liquefied.

[b] This possible ternary compound is uniaxial−, or has very small 2V; approx. indices of refraction ω-1.722, ϵ-1.715; twinning common with optic axis perpendicular to twinning.

tion of the diagram consists of the subordinate ternary system MgO-BeO-spinel with a ternary eutectic at 1,640° C and, by weight, approximately 44.4 percent of MgO, 27.5 percent of BeO, and 28.1 percent of Al_2O_3 (mole ratio $4MgO:4BeO:Al_2O_3$). This is supported by X-ray patterns of the mole compositions $4MgO:4BeO:Al_2O_3$ and $4MgO:16BeO:Al_2O_3$, which had been heated at 1,710° and 1,650° C, respectively. These patterns contained only the lines for periclase, bromellite, and spinel. However, a ternary compound may be the primary phase in a small portion of the system. Subordinate systems, if any, in the remainder of the diagram are obscured by solid-solution areas and by this ternary compound, which will be discussed further in connection with the fields of stability.

(a) FIELDS OF STABILITY

Results of fusion-point and softening-range observations, and petrographic and X-ray analyses of typical heated specimens, are summarized in table 4. These results are the basis for the location of field boundaries, as given in figure 6. Duplicate determinations were made whenever necessary, but the only tests reported in the table are those judged as typical or representative of best data. The values are not conclusive. In several instances it is obvious that equilibrium had not been reached, and the slow cooling in the furnace may have often destroyed any evidence of phases present at the liquidus.

It is believed that the primary field of MgO is substantially as shown, and that the field of BeO must be limited in part very nearly as shown by its boundaries with the MgO and $MgAl_2O_4$ fields. There is considerable doubt regarding the boundaries of the fields for $BeAl_2O_4$, Al_2O_3, and the postulated ternary compound.

It seems reasonably certain that a ternary compound is the primary phase in a small field approximately as indicated, that it melts incongruently, and that the compound composition is (in mole ratio) at or near $MgO:BeO:2Al_2O_3$. This supposedly ternary compound either is uniaxial or has a very small optic angle. The character is negative, twinning is common with the optic axis perpendicular to the twinning, and the indices of refraction are ω-1.722 to 1.725, ϵ-1.715 to 1.718. X-ray patterns for this phase in compositions $MgO:2BeO:2Al_2O_3$, $MgO:BeO:2Al_2O_3$, $MgO:2BeO:3Al_2O_3$, and $MgO:2BeO:Al_2O_3$ showed no significant shift from the lines given in table 5, such as would result if the phase were the result of solid solution. Nevertheless, the possibility remains that it is a solid solution. If the high indices of refraction of compositions along the spinel-chrysoberyl join are compared, there is apparently an almost continuous variation from chrysoberyl, through the new phase, to spinel. Also, as the crystal structures of $BeAl_2O_4$ and $MgAl_2O_4$ are similar, solid solution may be expected in this area.

The optical evidence that the field ascribed to the ternary compound extends into the MgO-BeO-spinel system is contradictory (test 198, table 4), but results of the fusion tests contain some evidence that the system BeO-spinel is not a simple one. Both $MgO:3BeO:Al_2O_3$ and $MgO:1.5BeO:Al_2O_3$ fused sharply at about 1,745° C, whereas the composition $MgO:2BeO:Al_2O_3$ fused from 10° to 15° C higher. This

relatively greater refractoriness of the 1:2:1 composition was not observed for these compositions when heated at lower temperatures (e. g. 1,700° C).

TABLE 5.—*Diffraction data from patterns for the dominant phase in compositions* $MgO:BeO:2Al_2O_3$ *and* $MgO:2BeO:2Al_2O_3$, *tests 352 and 355, table 4 (by H. F McMurdie)*

[VS=very strong, S=strong, M=medium, W=weak, VW=very weak]

Estimated intensity of lines	d	Estimated intensity of lines	d
	A		*A*
M	4.56	VS	2.03
M	4.22	VW	1.931
VW	4.05	M	1.875
W	3.25	VW	1.766
W	3.12	VW	1.717
VW	2.98	M	1.618
W	2.83	M	1.596
M	2.66	W	1.568
VW	2.56	W	1.535
VW	2.51	S	1.482
VS	2.40	VW	1.463
W	2.34	M	1.438
S	2.27	S	1.415
VW	2.18	M	1.362
M	2.09	W	1.322

(b) CERAMIC BODIES

The preparation of specimens for mechanical and electrical tests was limited to compositions that could be heated through a range of at least 25 deg C to produce a vitreous structure. Such compositions, when prepared and heated by the methods used in this study, are confined to the area lying between the BeO apex and the solid curved line in figure 6. Specimens of compositions in the remainder of the diagram either did not vitrify at the temperatures to which they were subjected, or passed from a porous (or underfired) condition to one in which they deformed under their own weight through a very short temperature range.[7] Vitrification ranges for the compositions prepared as test specimens are given in table 6. Although many of these compositions have long vitrification ranges, the shrinkage values indicate that the optimum maturing temperature producing the maximum density is in all cases in the upper portion of the range.

Specimens of six compositions were tested for strength in compression and for dielectric properties. Average values are given in table 7. From the data presented in table 2, and from the results for the specimens from tests 132–L and 181–L (table 7), it is evident that values obtained by crushing the pieces between porcelain blocks did not represent their full resistance to failure. It is unfortunate that the advantage of using cold-rolled steel was not discovered earlier in the investigation, and time did not permit repeating the work.

[7] It should be noted that ternary compositions containing more than 80 to 90 percent of Al_2O_3 are vitrifiable according to patent literature [18] but they were not prepared in this investigation.

TABLE 6.—*Temperature range in which* MgO-BeO-Al_2O_3 *specimens attained an absorption of less than 0.1 percent, and resultant linear shrinkage*

Composition (mole)			Vitrification range		Shrinkage range
MgO	BeO	Al_2O_3	1[a]	2[b]	
			°C	°C	%
1	24	1	1,600 to 1,725	[c] 1,625	15.5 to 17.6
1	16	1	1,600 to 1,725	None	15.5 to 16.5
1	8	1	1,625 to 1,725	------do------	13.6 to 14.4
1	4	1	1,680 to 1,725	----------	11.2 to 12.0
1	2	1	[d] 1,650	None	9.7
4	96	1	1,500 to 1,635	1,500 to 1,625	17.9 to 20.0
4	48	1	1,500 to 1,635	1,500 to 1,625	16.8 to 19.4
4	24	1	1,600 to 1,630	1,500 to 1,625	14.4 to 20.5
4	16	1	[c] 1,630	1,500 to 1,600	15.5 to 20.0
4	8	1	None	1,560 to 1,600	21.6 to 22.2
2	4	1	[c] 1,600	----------	13.0

[a] Specimens made with fused magnesia and commercial alumina.
[b] Specimens made with calcined magnesia and laboratory prepared alumina.
[c] Not vitreous when heated 25° C above or below this temperature.
[d] Overfired at 1,700° C.
[e] Partly fused at 1,650° C.

The dielectric tests show interestingly low power losses in some cases. Values for electrical resistivity (T, value) and relative thermal conductivity are given in table 8. The trend is for both electrical resistivity and thermal conductivity to increase with increase in the BeO content. Values for the specimens from test 27–L indicate that electrical resistivity may be relatively greater for a composition when heated above the vitrification range, and having an "overfired" and porous structure, than for comparable pieces heated to vitrification. Compared with conventional feldspathic porcelains [19, 20], the thermal expansion is high for all of the compositions tested (table 9).

TABLE 7.—*Resistance to crushing, and dielectric properties, of typical compositions in the* MgO-BeO-Al_2O_3 *system*

[Specimens made with fused magnesia and commercial alumina]

Specimen from test No.	Composition (mole)			Matured at—	Number of specimens	Absorption	Compressive strength [a]	Number of specimens	Absorption	Dielectric properties at 100 kc [b]	
	MgO	BeO	Al_2O_3							Constant	Loss angle
				°C		%	lb/in.²		%	K	tan δ
84–L	1	24	1	1,725				3	0.04	6.8	0.002
132–L	1	24	1	1,725	3	0.01	169,000				
160–L	1	24	1	1,600				1	.01	6.7	.006
181–L	1	24	1	1,650	3	.00	[c] 286,000	2	.00	6.9	.004
85–L	1	8	1	1,725	3	.03	152,000	2	.04	6.8	.001
86–L, 94–L	1	4	1	1,725	3	.04	142,000	2	.07	6.5	.002
87–L	4	96	1	1,630	3	.06	105,000				
91–L	4	96	1	1,635	3	.02	144,000	2	.04	6.6	.003
88–L	4	24	1	1,630	2	.06	137,000				
95–L	4	24	1	1,630	3	.04	129,000	2	.04	6.9	.070
93–L	4	8	1	1,635	3	.24	136,000	2	.34	7.7	.021

[a] The contact blocks between the specimens and the press platens were porcelain in all cases except for specimens from test 181–L, in which case cold-rolled steel was used (see table 2).
[b] The dielectric values were determined by C. M. Sparks and A. H. Scott.

TABLE 8.—*Electrical resistivity (T_e value) and relative thermal conductivity of compositions in the* MgO-BeO-Al_2O_3 *system (each value represents one specimen)*

[Specimens made with fused magnesia and commercial alumina]

Specimen from test No.	Composition (mole)			Matured at—	Absorption	Electrical resistivity [a] (T_e value)	Absorption	Thermal conductivity [b]
	MgO	BeO	Al_2O_3					
				°C	%	°C.	%	
76-L	4	96	1	1,635	0.01	1,190	0.01	11
194	4	96	1	1,655	.06	1,195		
80-L	4	48	1	1,630	.09	1,180	.00	11
179	4	48	1	1,655	.01	1,178		
78-L	4	24	1	1,630	.01	1,161	.01	12.5
156	4	24	1	1,645	.30	1,166		
79-L	4	16	1	1,630	.03	1,156	.03	9
37-L	4	16	1	1,660	.10	1,190		
76-L	4	16	1	1,635	.02	1,161		
213	4	8	1	1,625	.30	1,110	.32	7
217	4	8	1	1,640	.26	1,127		
218	4	8	1	1,630	.31	1,106		
76-L	4	4	1	1,635	.19	1,140	.19	3
139	4	4	1	1,640	.40	1,142		
217	4	4	1	1,640	.35	1,127		
218	4	4	1	1,630	.35	1,106		
241	1	24	1	1,720			.01	11
82-L	1	24	1	1,725	.01	1,137	.01	9
27-L	1	24	1	1,775	1.50	1,210		
189	1	24	1	1,720	0.10	1,150		
61-L	1	16	1	1,735			.01	8
82-L	1	16	1	1,725	.01	1,136	.01	6
27-L	1	16	1	1,775	1.50	1,200		
152	1	16	1	1,740	0.70	1,131		
158	1	16	1	1,720	.06	1,185		
82-L	1	8	1	1,725	.02	1,125	.02	5
167	1	8	1	1,720	.06	1,155		
86-L	1	4	1	1,720	.03	1,124	.03	4
83-L	1	4	1	1,725	.04	1,134		

[a] The T_e value for electrical resistivity is the temperature at which, by calculation based on test values, a 1-cm cube of the material has a resistance of 1 megohm. The values were obtained by E. N. Bunting.

[b] These values are the reciprocal, multiplied by 100, of the temperature drop through a 0.5-in. height of specimen approximately ½ in. in diameter. The values were determined by E. N. Bunting.

In general, it may be said that compositions over a wide range in the MgO-BeO-Al_2O_3 system show interesting possibilities as vitreous ceramic bodies. Specimens developed very high strength in compression and, even when tested under conditions that were not the most advantageous, the values ranged from 105,000 to 169,000 lb/in.^{2} This compares very favorably, for example, with values obtained for commercially prepared unglazed specimens of high-tension insulator porcelains [20], which ranged from 27,000 to 88,000 lb/in.^{2} in compressive strength. The electrical resistivities compare favorably with those for various types of spark-plug insulator compositions which, as published by Riddle [21], range in Te value from 632° to 1,066° C. The dielectric properties are good, and the thermal conductivity will range from about that of a commercial high-alumina body to practically the conductivity of a vitreous specimen of BeO, which is three to four times greater than that of the alumina body.

TABLE 9.—*Linear thermal expansion data*

Specimen from test No.	Composition (mole)					Coefficient $\times 10^6$									Expansion to 1,000° C
	MgO	BeO	Al_2O_3	ThO_2	ZrO_2	Room temp. to 100° C	100° to 200°	200° to 300°	300° to 400°	400° to 500°	500° to 600°	600° to 700°	700° to 800°	800° to 900°	900° to 1,000°	
																%
139	8	4	1	------	------	7.0	8.7	9.6	8.2	10.5	11.1	10.4	10.8	9.4	9.3	0.920
27-L	4	96	1	------	------	5.3	7.0	7.7	8.7	9.6	9.2	10.0	10.3	9.2	------	.788
40-L	4	4	1	------	------	5.6	6.7	7.8	8.8	9.4	10.5	8.5	10.1	11.0	9.5	.851
27-L	1	16	1	------	------	5.2	6.7	7.9	8.7	9.5	9.8	9.8	10.5	10.9	9.9	.870
137	1	4	1	------	------	5.4	6.7	8.5	8.1	9.8	9.7	9.3	9.4	9.5	9.1	.862
54-L	1	1	4	------	------	5.2	7.0	8.0	8.1	9.6	8.8	8.7	9.2	10.0	9.5	.838
183-L	------	48	1	1	------	4.4	7.0	6.9	7.8	9.3	9.7	9.0	10.0	9.6	------	.729
183-L	------	12	1	1	------	5.4	7.3	8.2	8.7	9.4	9.7	10.1	10.7	10.4	9.1	.871
182-L	------	160	2	1	------	4.7	6.7	8.2	7.9	7.9	9.7	10.0	10.4	10.2	------	.745
182-L	------	24	2	1	------	5.3	7.1	8.1	8.5	9.4	9.6	10.5	9.7	11.0	9.9	.870
182-L	------	48	4	1	------	4.8	7.1	8.0	8.6	9.8	9.5	9.7	11.9	10.0	------	.799
182-L	------	18	4	1	------	5.2	7.0	7.8	8.5	9.5	9.0	9.0	10.5	9.7	9.7	.846
171-L	------	48	10	1	------	4.8	6.9	8.1	8.2	8.6	8.6	9.2	10.1	8.6	------	.774
278	------	4	4	1	------	5.4	7.1	6.8	8.5	9.1	9.1	8.9	9.8	9.3	9.4	.859
173-L	------	8	1	------	2	5.2	6.9	7.8	8.2	9.0	8.9	8.9	9.3	9.7	8.3	.840

[a] Expansion to 900° only.

(c) REACTION WITH WATER

A limited number of pieces were tested as indicated in table 10 in order to obtain some relative numerical values for the resistance of nonvitreous specimens to the action of water. The data show that some "hydrolysis" (weight retained after drying at 110° C) and solution (loss in weight after heating at 800° C) had resulted. Although not serious in most cases, it was thought sufficient to justify the procedure of boiling in CCl_4.

TABLE 10—*Effect of boiling fired specimens of* MgO-BeO-Al_2O_3 *compositions in water*

Specimen from test No.	Composition (mole)			Absorption [a]	Specimens boiled in water for 5 hr	
	MgO	BeO	Al_2O_3		Gain in weight after redrying at 110° C	Change in weight after redrying at 800° C
				%	%	%
37-L	4	96	1	1.35	0.025	−0.008
166	4	96	1	0.93	.12	−.013
166	4	96	1	.15	.04	−.021
37-L	4	48	1	1.44	.05	−.013
37-L	4	16	1	0.10	.005	−.018
156	4	24	1	.34	.06	−.03
36-L	4	8	1	[b]	----------	[c]
154	4	8	1	1.14	.23	−.01
40-L	4	8	1	1.02	.28	−.05
40-L	4	4	1	0.23	.11	+.02
40-L	4	2	1	3.13	1.16	+.05

[a] Based on weight of specimen after boiling and after redrying at 800° C
[b] Porous.
[c] Disintegrated.

5. THE SYSTEM CaO-BeO-Al_2O_3

The subordinate binary system CaO-BeO is apparently free from solid solution. Wartenburg and coworkers [16] reported the eutectic at about 1,450° C and 50 wt percent of CaO. In this investigation, the eutectic was found at 1,405° C and approximately 65 wt percent of CaO. Compositions between CaO and CaO:BeO (or 100 percent and 69.2 percent of CaO by weight) contained CaO in well-defined cubes of refractive index 1.84 as the primary phase. The matrix was isotropic with a refractive index of 1.64. Compositions between CaO:1.5BeO and BeO (or 59.9 percent and zero percent of CaO by weight) showed well-crystallized BeO as the primary phase. The addition of 1 percent by weight of CaO to BeO made it possible to obtain nonabsorbent specimens as low as 1,375° C and the vitrification range extended to over 1,500° C.

Only a relatively small number of bodies in the ternary system were investigated. The results indicate that some advantage would be gained over the corresponding MgO-BeO-Al_2O_3 system so far as the temperatures required for vitrification are concerned. For example, five ternary compositions containing 70 percent or more of BeO, and from 5 to 20 percent of CaO, vitrified between 1,400° and 1,500° C. In general, the texture was coarsely crystalline, and no tests of mechanical strength or thermal and electrical properties were made.

6. THE SYSTEM BaO-BeO

Specimens ranging in mole composition from BaO:BeO to BaO:12BeO (85.97 percent to 33.81 percent by weight of BaO) were heated at 1,170°, 1,250°, 1,300°, and 1,400° C. They were placed on BeO in the kiln because the first trials had shown reaction with platinum. At 1,170° C the 1:1 mixture fused partly and the 1:2 mixture became sintered. At 1,400°, the 1:1 and 1:2 mixtures fused completely, the 1:3 was bloated, and the 1:6 and 1:12 specimens appeared vitreous, coarse-grained, and were medium gray in color. BeO crystals, and the absence of free BaO, characterized all the heated samples. An unidentified phase at the high-BaO end of the series is probably orthorhombic, with $2V=90°$, and the refractive index is slightly above 1.77. At the high-BeO end another unidentified phase appears to be monoclinic. It is biaxial negative, $2V=75°$, and the refractive indices are $\gamma=1.77$, $\beta=1.768(?)$, $\alpha=1.764$. Extinction is oblique, and its two cleavages are at an angle of 78°. This system may be complicated by a low-temperature eutectic between BaO and $BaCO_3$ [24].

The preparation of specimens for mechanical or electrical tests was not attempted.

7. THE SYSTEM BeO-Al_2O_3-ThO_2

This is a distinctly high-temperature system. Thoria is described [22] as fusing at about 3,000° C. It is a cubic compound with the very high refractive index of $2.20\pm$, as given by Larsen [23]. In the specimens examined it occurred generally as rounded or angular grains, as rods, or as spherules. It was not observed in the cubic habit. The other end members of the system, BeO and Al_2O_3, fuse at about 2,520° C [16] and 2,015° ±15° C [12], respectively. The lowest liquidus point in the ThO_2-BeO system is reported [16] to be at 2,200° C and about 20 percent by weight of BeO. In this study,

the lowest melting eutectic in the BeO-Al_2O_3 system was placed at 1,865° C (fig. 6).

According to the results of this investigation, the Al_2O_3-ThO_2 eutectic is at 1,910° C and 60.7 wt percent of Al_2O_3 or, in mole ratio, at $4Al_2O_3$:ThO_2, which is in good agreement with the findings of Wartenburg and Reusch [15]. The location of the eutectic (fig. 7)

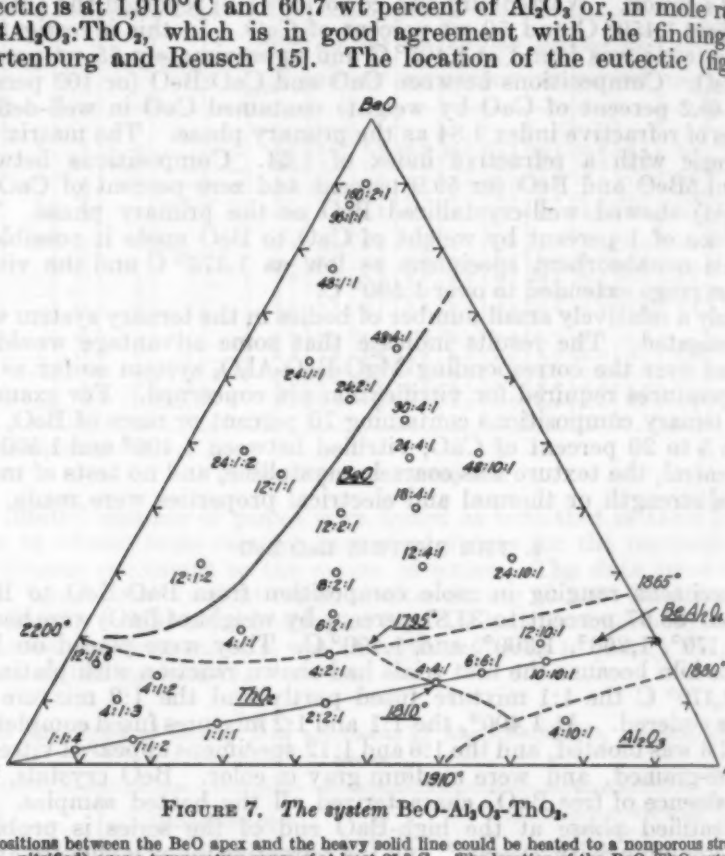

FIGURE 7. *The system* BeO-Al_2O_3-ThO_2.

Compositions between the BeO apex and the heavy solid line could be heated to a nonporous structure (i. e., vitrified) over a temperature range of at least 25 ° C. The location of the BeO-ThO_2 eutectic is taken from H. v. Wartenburg and H. J. Reusch, Z. anorg. allgem. Chem. **207**, 1(1932).

is based on fusion tests entirely, as microscopic examinations (table 11) showed no differences in texture that were useful for that purpose. The intergrowth texture in fused specimens of Al_2O_3:$2ThO_2$, Al_2O_3:ThO_2, $2Al_2O_3$:ThO_2, and $3Al_2O_3$:ThO_2 may result from solid solution at high temperatures, and unmixing during cooling, but the evidence is not conclusive.

The thermal reactions in most of the mixtures of ThO_2 and Al_2O_3, and also in mixtures along the chrysoberyl-thoria tie-line, are characterized by the formation of very low viscosity liquids, as evidenced (1) by the rapidity with which softening and flow progressed when the solidus temperature was exceeded, (2) by the fact that beginning of fusion was clearly defined and was within a few degrees of the pertinent eutectic temperature, and (3) by the literal disappearance of Al_2O_3 test pieces into the pores of the ThO_2 shapes upon which the pieces had been supported whenever they were heated above the Al_2O_3-ThO_2 eutectic temperature.

The results of fusion tests and microscopic examinations agree with the assumption that a simple system exists between chrysoberyl ($BeAl_2O_4$) and thoria, with limited solid solution at some higher temperature, as indicated by "exsolution" texture. Nearly the entire ternary system is therefore, on a weight basis, occupied by the subordinate system BeO-$BeAl_2O_4$-ThO_2. Compositions in the $BeAl_2O_4$-ThO_2 system (fig. 7), varying in ThO_2 content from about 25 to 80 percent, all fused within a range of ± 10 deg C. The eutectic in this system was placed at 1,810° C and $4BeO:4Al_2O_3:ThO_2$, partly because of the proximity of this composition to the Al_2O_3-ThO_2 eutectic, partly because of an apparently higher liquidus on either side, and in spite of the sharp fusion at 1,800° to 1,805° of the compositions $BeO:Al_2O_3:2ThO_2$ and $BeO:Al_2O_3:ThO_2$. There is no logical explanation from the data for this fusion behavior of the 1:1:2 and 1:1:1 mixtures. The lowest ternary eutectic is believed to be at 1,795° C and near the mole composition $4BeO:2Al_2O_3:ThO_2$.

(a) FIELDS OF STABILITY

The fields of stability of the primary phases and the critical temperatures are believed to be very nearly as shown in figure 7, based on the information given in table 11. There appears to be limited solid solution between ThO_2 and $BeAl_2O_4$, as mentioned previously, and from the chrysoberyl end of this binary system the solid-solution seems to extend toward the Al_2O_3 apex so as to include the mole composition $4BeO:10Al_2O_3:ThO_2$.

(b) CERAMIC BODIES

It is possible to vitrify most of the compositions in the BeO field of the BeO-$BeAl_2O_4$-ThO_2 system, but the temperature range through which a nonporous structure can be obtained is greatest near the BeO apex. This range decreases rapidly with increase in alumina content and more gradually with increase in thoria content. Only those ternary compositions between the BeO apex and the solid curved line in figure 7 were vitrified over a range of at least 25 deg C. The optimum temperature interval in which to produce nonporous specimens was from 1,600° to 1,750° C. Several compositions on the opposite side of the solid curved line were vitrified by heating at 1,700° C and three (1:1:2, 4:4:1 and 12:10:1) by heating at 1,750° C. No significant differences in vitrification behavior were observed between specimens made with calcined thoria and those made with fused thoria.

Good strength in compression was obtained with the mole compositions $160BeO:2Al_2O_3:ThO_2$ and $48BeO:Al_2O_3:ThO_2$. The former, when matured at 1,725° C, and the latter at 1,750° C, showed less than 0.02-percent absorption. The specimens were crushed between cold-rolled steel blocks and gave average values of 244,000 lb/in.^{2} for the 160:2:1 mix and 279,000 lb/in.^{2} for the 48:1:1 mix. Minimum values for individual specimens of the two compositions were 240,000 and 274,000 lb/in.^{2}, respectively. These bodies also had promising power-loss values of less than 0.01 percent at 100 kc/s, and the K value ranged between 7 and 8. Coefficients of linear thermal expansion for the 160:2:1 mix, and for other compositions in this system, are given in table 9. Values for electrical resistivity and thermal conductivity are given in table 12.

TABLE 11.—*Results of fusion tests and softening range determinations, and X-ray and microscopical examinations, of the specimens in the system* BeO-Al_2O_3-ThO_2

Test No.	Composition						Heated at (max).—	Effect of heating (temperatures in degrees centegrade)	Results of X-ray and microscopical examinations. (Specimens examined were not quenched and the phases observed may not be those in equilibrium at the maximum temperature of heating or at the liquidus)
	Mole			Weight					
	BeO	Al_2O_3	ThO_2	BeO	Al_2O_3	ThO_2			
				%	%	%	°C		
363	.....	1	2	.....	16.15	83.75	1,925	Fusion incomplete; started at 1,910°	Thoria as rounded grains is the major constituent. Remainder is interstitial alumina, angular ThO_2, and ThO_2 in intergrowth texture.
374	.....	1	1	.....	27.80	72.20	1,915	Fusion complete •; started at 1,910°	Thoria as rounded grains and in intergrowth texture. Alumina is interstitial to the thoria.
365	.....	2	1	.....	43.55	56.45	1,920	Fusion complete; started at 1,905°	Thoria occurs as rounded grains and intergrowth texture in a matrix of alumina.
367	.....	3	1	.....	53.65	46.35	1,915	Fusion complete; started at 1,910°	Do.
366	.....	4	1	.....	60.70	39.30	1,910	Complete fusion at this temperature	No intergrowth texture. ThO_2 and Al_2O_3 present as irregular and as rounded grains.
364	.....	6	1	.....	69.85	30.15	1,915	Fusion complete; started at 1,910°	Alumina in large angular grains and thoria in relatively small angular grains.
376	.....	10	1	.....	79.40	20.60	1,935	Fusion far from complete; started at 1,920°	
389	12	1	6	15.10	5.13	79.77	1,935	Vitreous. Little if any softening.	
370	1	1	4	2.1	8.6	89.3	1,900	Fusion incomplete; started at 1,805°	About 95 percent of thoria, and 5 percent of chrysoberyl containing thoria in intergrowth texture.
446	4	1	3	10.05	10.25	79.70	1,875	Fusion incomplete; started at 1,820°.	
442	24	1	2	48.8	8.3	42.9	1,925	No softening	BeO as blocky grains 20 to 30 microns in diameter, thoria as angular fragments 1 to 20 microns in size, and chrysoberyl very rare.
381	12	1	2	32.25	10.95	56.80	1,925	Fusion far from complete; started at 1,865°	BeO and ThO_2, mostly as blocky and irregular grains. No $BeAl_2O_4$ noted.
382	4	1	2	13.70	13.95	72.35	1,875	Fusion incomplete; started at 1,835°	Rounded grains of ThO_2 are surrounded by a very fine-grained intergrowth texture of ThO_2 in BeO. Angular fragments of ThO_2, and a few grains of $BeAl_2O_4$ also present.
359	1	1	2	3.80	15.55	80.65	1,805	Fused quickly at 1,800°	Thoria, both in rounded grains and intergrowth texture, and interstitial chrysoberyl.
297-L	96	1	1	86.80	3.65	9.55	1,800	No softening.	
312-L	48	1	1	76.6	6.5	16.9	1,800	.....do	
388	24	1	1	62.15	10.55	27.30	1,935	Fusion far from complete	Only beryllia and thoria were identified.
308	12	1	1	45.1	15.3	39.6	1,905	Fusion incomplete; started at about 1,825°	BeO as prismatic or lath-shaped crystals, in some cases containing rounded grains of thoria. Thoria in rounded and angular grains.
384	4	1	1	21.45	21.85	56.70	1,875	Fusion well advanced; started at 1,840°	BeO interstitial to rounded and angular grains of ThO_2. [illegible] and $BeAl_2O_4$.
313	160	2	1	90.00	4.35	5.65	1,850	No softening.	
377	24	2	1	56.2	19.1	24.7	1,900	Fusion far from complete; started at 1,835°	BeO in lath-shaped and irregular grains. ThO_2 in rounded grains, both free and as inclusions in BeO. Occasional

384	4	1	1	21.45	21.85	56.70	1,875	Fusion well advanced; started at 1,840°.	and angular grains. BeO interstitial to rounded and angular grains of ThO_2. Large crystals of $BeAl_2O_4$ in the form of the mineral chrysoberyl and $BeAl_2O_4$.
313	160	2	1	90.00	4.35	5.65	1,850	No softening.	
377	24	2	1	56.2	19.1	24.7	1,900	Fusion far from complete; started at 1,835°.	BeO in lath-shaped and irregular grains. ThO_2 in rounded grains, both free and as inclusions in BeO. Occasional grains of chrysoberyl. X-ray pattern has lines for BeO and ThO_2 only.
386	12	2	1	39.1	26.5	34.4	1,860	Fusion incomplete; started at 1,845°.	Largely ThO_2 as rounded grains, and as both coarse and fine intergrowth with BeO. No $BeAl_2O_4$ identified.
444	8	2	1	30.0	30.5	39.5	1,875	Fusion incomplete; started at 1,820°.	
387	6	2	1	24.3	33.0	42.7	1,845	Fusion not complete; softened rapidly above 1,835°.	BeO is interstitial to ThO_2, which occurs as rounded grains and in intergrowth texture.
391	4	2	1	17.6	35.9	46.5	1,805	Fusion almost complete, advanced rapidly above 1795°.	ThO_2, BeO, and $BeAl_2O_4$ in coarse and fine intergrowth texture.
331	2	2	1	9.7	39.1	51.2	1,820	Completely fused; started at 1,810°.	Characterized by large twinned crystals of chrysoberyl with thoria in parallel arrangement of minute rods.
380	48	4	1	64.1	21.8	14.1	1,920	Incipient fusion.	Beryllia in blocky grains containing inclusions of thoria. No chrysoberyl identified.
176–L	30	4	1	52.80	28.55	18.55	1,750	No softening.	
379	24	4	1	47.20	32.05	20.75	1,925	Fusion well advanced; started about 1,850°.	Very similar to specimen from test 377.
196–L	18	4	1	40.10	36.35	23.55	1,750	No softening.	
357	12	4	1	30.90	41.95	27.15	1,905	Fusion well advanced; started at 1,870°.	Principal phases are BeO and $BeAl_2O_4$. ThO_2 occurs as parallel arranged inclusions in the BeO and as rounded particles in the $BeAl_2O_4$.
207–L	4	4	1	12.95	52.55	34.20	1,810	Fused sharply at 1,810°.	Chrysoberyl as blocky crystals with ThO_2 inclusions in various forms (rods, amoeboid and rounded grains.) Exsolution texture is present in about one-third of the $BeAl_2O_4$.
353	6	6	1	14.65	59.60	25.75	1,815	Complete fusion between 1,810° and 1,815°.	Some chrysoberyl in large plates. Otherwise similar to specimen from test 207–L.
176–L	48	10	1	48.35	41.00	10.65	1,750	No softening.	
449	24	10	1	31.9	54.1	14.0	1,900	Fusion incomplete; started at 1,810°.	Large (0.5 to 1.0 mm) crystals of $BeAl_2O_4$. ThO_2 occurs as rounded parallel rods and amoeboid grains in the chrysoberyl. BeO present, but rare.
448	12	10	1	19.0	64.3	16.7	1,840	Fusion complete; started at 1,800°.	Chrystal phases similar to specimen from test 449. X-ray pattern shows lines for $BeAl_2O_4$ and ThO_2.
354	10	10	1	16.33	66.43	17.24	1,850	Fusion complete; started at 1,825°.	Some large plates of chrysoberyl but all $BeAl_2O_4$ crystals contain ThO_2 in exsolution texture. May be in a solid-solution area.
447	4	10	1	7.2	73.7	19.1	1,850	Fusion far from complete; started at 1,820°.	Large platy crystals of $BeAl_2O_4$ containing amoeboid grains of ThO_2 in parallel orientation. Main portion of sample is chrysoberyl and thoria in equigranular formation. No corundum could be found. The X-ray pattern also contains no lines for Al_2O_3 but shows a slight shift in the lines for chrysoberyl. May be in a solid-solution area.

• The term "complete fusion" means that the pyramidal specimen had fused sufficiently to flow into a flat button shape, and does not necessarily connote that the mixture had completely liquefied.

TABLE 12.—*Absorption, electrical resistivity (T_e value) and relative thermal conductivity of compositions in the system* BeO-Al_2O_3-ThO_2 *(each value represents 1 specimen)*

Specimen from test No.	Composition (mole)			Matured at—	Absorption	Electrical resistivity [a] (T_e value)	Thermal conductivity [b]
	BeO	Al_2O_3	ThO_2				
				°C	*Percent*	°C	
320-L	12	1	2	1,700	0.00		
204-L	12	1	2	1,700	.02	767	
300-L	24	1	1	1,750	.02		
233-L	24	1	1	1,650	.01	945	
191-L	12	1	1	1,700	.00		
195-L	12	1	1	1,750	.01	910	
254-L	160	2	1	1,650	.00		
197-L	24	2	1	1,675	.00		
175-L	24	2	1	1,700	.01	1,005	
175-L	24	2	1	1,700	.01	1,076	
320-L	12	4	1	1,700	.00		
191-L	12	4	1	1,700	.01	904	
175-L	48	10	1	1,700	.11		
191-L	48	10	1	1,700	.02	1,135	
320-L	24	10	1	1,700	.00		
191-L	24	10	1	1,700	.02	1,057	
453	12	10	1	1,750	.01		
195-L	12	10	1	1,750	.01	968	
258			1	2,040	1.90	490	

[a] The T_e value for electrical resistivity is the termperature at which by calculation based on test values a 1-cm cube of the material has a resistance of 1 megohm. These values were obtained by E. N. Bunting.
[b] These values are the reciprocal, multiplied by 100, of the temperature drop through a 0.5-in. height of specimen approximately 0.5 in. in diameter, and were determined by E. N. Bunting.

8. THE SYSTEM BeO-Al_2O_3-ZrO_2

The phase relations in this system (fig. 8) are, in all probability, much like those in the system BeO-Al_2O_3-ThO_2. The evidence points to a simple binary relation between chrysoberyl and zirconia, with the possibility of limited solid solution (table 13). As a generalization, one can say that the beginning of fusion of the ternary mixtures will average about 50 deg C lower than for corresponding mixtures in the BeO-Al_2O_3-ThO_2 system, but the binary eutectics of the end members are about the same in the two systems. The eutectic between Al_2O_3 and ZrO_2 at about 50 mole percent, or 55 wt percent, of ZrO_2 has been reported at 1,920° C [25] and at 1,900° C [15]. In this study, fusion was observed at 1,885° C. For the system BeO-ZrO_2, a compound ($3BeO{:}2ZrO_2$) and two eutectics were reported in 1930 [26], but a year later a single eutectic at about 75 wt percent of ZrO_2 and 2,240° C was reported [27]. In the present study, no evidence was found of a compound between BeO and ZrO_2.

(a) FIELDS OF STABILITY

The fusion data in table 13 indicate that the various stability fields are as presented in figure 8. Both the ternary eutectic for beryllia, zirconia, and chrysoberyl, and the binary eutectic for zirconia and chrysoberyl, are believed to be very nearly as shown. These points, together with the eutectics in the binary systems of the end members, serve to approximate the location of the field boundaries. The least certain is the location of the boundary between the fields of chrysoberyl and Al_2O_3.

The dotted line (fig. 8) encloses a group of compositions, all of which contained an exsolution texture after having been heated at or

near the fusion temperature. This exsolution texture is evidence of some degree of solid solution. Within this area, ZrO_2 occurs partly as rods or as amoeboid and graphic forms in chrysoberyl. Tetragonal zirconia in the exsolution texture may invert in part to the monoclinic form during cooling, and some amoeboid grains of tetragonal ZrO_2 contain lathlike crystals of lower refractive index and higher birefringence than the enclosing grains. This evidence is assumed to indicate that solid solution and exsolution occur within the range of temperatures in which tetragonal ZrO_2 is the stable phase, probably between 1,000° and 1,500° C [12].

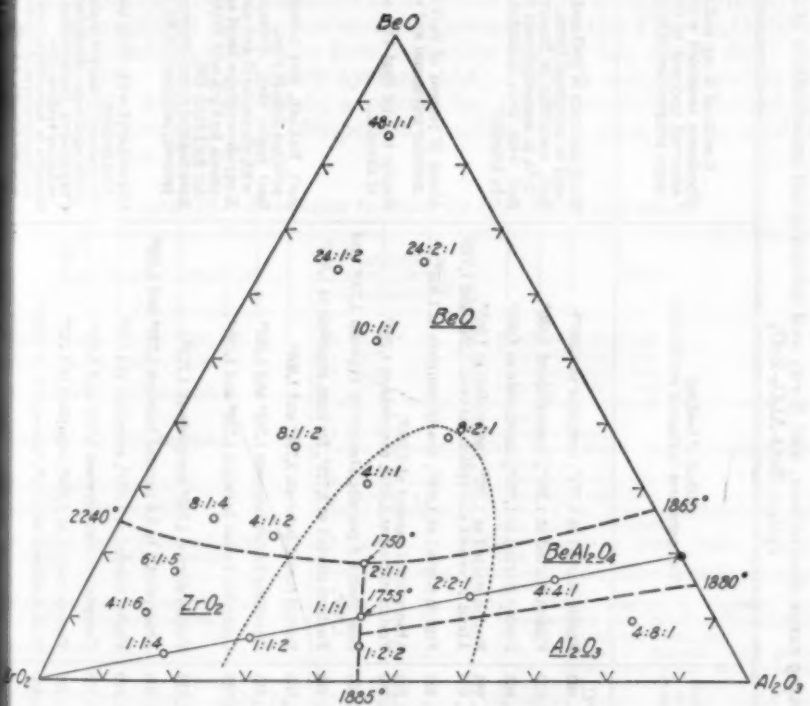

FIGURE 8. *The system* $BeO\text{-}Al_2O_3\text{-}ZrO_2$.

No composition in this system was vitrified. The location of the $BeO\text{-}ZrO_2$ eutectic is taken from H. v Wartenburg and W. Gurr, Z. anorg. allgem. Chem. **196**, 374 (1931).

(b) CERAMIC BODIES

No composition in this system became vitrified (i. e., had less than 0.1-percent absorption) at any of the temperatures to which it was heated. These temperatures ranged from 1,600° to 1,800° C. Only one composition, mole ratio $48BeO:Al_2O_3:ZrO_2$, attained an absorption of less than one-half percent (table 13). No specimens were prepared for mechanical strength or for electrical tests, but the thermal expansion data are given in table 9 for one specimen with an absorption of 1.4 percent. The T_s value for a specimen of ZrO_2, with an absorption of 2.3 percent after having been heated at 1,900° C, was 421, and the thermal conductivity value (see footnote "b", table 12) for the same specimen was 1.4.

TABLE 13.—*Results of fusion point and softening range observations, and X-ray and microscopical examinations of the tested specimens in the system* $BeO-Al_2O_3-ZrO_2$

Test No.	Composition						Heat at (max)—	Effect of heating (Temperatures in degrees centigrade)	Results of X-ray and microscopical examinations (Specimens examined were not quenched and the phases observed may not be those in equilibrium at the maximum temperature of heating or at the liquidus)
	Mole			Weight					
	BeO	Al_2O_3	ZrO_2	BeO	Al_2O_3	ZrO_2			
	%	%	%	%	%	%	°C		
432	4	1	6	10.6	10.8	78.6	1,890	Fusion started at 1,775°, complete at 1,890°.	Small amounts of BeO and of $BeAl_2O_4$. ZrO_2 in monoclinic and in tetragonal forms.
329	6	1	5	17.3	11.7	71.0	1,850	Fusion started at 1,780°, incomplete at 1,850°.	BeO, occurring in blocky grains, is rare. Remainder is ZrO_2 in monoclinic and tetragonal forms.
430	8	1	4	25.2	12.8	62.0	1,865	Fusion started at 1,780°, incomplete at 1,865°.	BeO with ZrO_2 inclusions. ZrO_2 is uniaxial (+?), may be trigonal.
429	1	1	4	4.0	16.5	79.5	1,865	Fusion started at 1,765°, incomplete at 1,865°.	
(•)	24	1	2	63.3	10.7	26.0	1,800	About 1-percent absorption between 1,650° and 1,775°.	
336	8	1	2	36.5	18.5	45.0	1,825	Fusion started at 1,800°, nearly complete at 1,825°.	About 20 percent of BeO in laths and irregular grains, remainder tetragonal and monoclinic ZrO_2.
(•)	4	1	2	22.3	22.7	55.0	1,750	Absorption 1 percent at 1,700°.	
431	1	1	2	6.7	27.3	66.0	1,780	Fusion started at 1,760°, complete at 1,780°.	Similar to 1:1:1 (test 433), except for larger relative quantity of zirconia.
(•)	48	1	1	84.2	7.1	8.7	1,750	Less than 0.5 percent absorption between 1,700° and 1,750°.	
434	10	1	1	52.6	21.5	25.9	1,875	Fushion started at 1,775°, far from complete at 1,875°.	
332	4	1	1	30.7	31.4	37.9	1,800	Partial fusion between 1,795° and 1,800°.	BeO, $BeAl_2O_4$, and tetragonal and monoclinic ZrO_2. Exsolution texture rare.
436	2	1	1	18.2	37.0	44.8	1,755	Complete fusion between 1,745° and 1,755°.	BeO grains rare. Tetragonal ZrO_2 in exsolution texture with chrysoberyl and also as rounded monoclinic grains.
433	1	1	1	10.0	40.7	49.3	1,760	Complete fusion between 1,755° and 1,760°.	X-ray shows chrysoberyl and monoclinic ZrO_2. Microscope shows $BeAl_2O_4$ and ZrO_2 present in texture, as described for 2:1:1 (test 436).
437	1	2	2	5.3	42.9	51.8	1,775	Fusion started 1,765° complete at 1,775°.	Rare isolated grains of corundum. Chrysoberyl and zirconia present, as described for 2:1:1 (test 436).
(•)	24	2	1	64.8	22.0	13.2	1,800	Absorption 1 to 1.4 percent between 1,725° and 1,800°.	
327	8	2	1	38.0	38.7	23.3	1,870	Fusion started at 1,820°, complete at 1,870°.	Chrysoberyl with ZrO_2 inclusions, BeO rare, some exsolution texture.
326	2	2	1	13.2	54.1	32.7	1,765	Complete fusion between 1,760° and 1,765°.	Chrysoberyl, rounded grains of ZrO_2 which are mostly monoclinic, and some chrysoberyl-zirconia exsolution texture.
438	4	4	1	15.8	64.6	19.6	1,795	Fusion started at 1,765°, complete at 1,795°.	Chrysoberyl predominant, ZrO_2 *mostly* monoclinic, exsolution texture rare.
435	4	8	1	9.6	78.5	11.9	1,850	Fusion started at 1,785°, incomplete at 1,850°.	Zirconia in monoclinic form as inclusions in, and interstitial to, large grains of chrysoberyl which has refractive indices α=1.746, β=1.743, γ=1.748.

9. RESISTANCE TO ATTACK BY PbO

The results of a limited number of tests to determine relative resistance to the attack of PbO, and made as described in section III, are summarized in table 14. The tests show (a) that attack on specimens immersed in molten PbO is much greater than on specimens exposed to PbO vapor, (b) that attack at 1,100° C is much greater than at 1,000° C, and (c) that, of the specimens tested, the siliceous bodies were the least resistant and the "high BeO" compositions were the most resistant.

The relatively low resistance of siliceous bodies of the mullite type may be explained by the low-melting eutectics in the PbO-Al_2O_3-SiO_2 system, in which there are four eutectics within the range 694° to 704° C [28]. In the binary system Al_2O_3-PbO, a eutectic occurs at 865° C [28], which no doubt accounts for the appreciable solution of the Al_2O_3 specimen of 99.95-percent purity. No data are available for the system PbO-BeO.

TABLE 14.—*Resistance to attack by PbO liquid and vapor*

Composition and absorption	Treatment for 4 hr at 1,100° C, except as noted	Result
Commercial A, mullite type	In vapor *	1.1-percent weight loss.
Commercial B, mullite type	do *	0.3-percent weight loss.
Commercial B, high alumina	In vapor	7.4-percent weight loss.
	do	5.5-percent weight loss.
Commercial C, high alumina	Partly immersed	Severe attack; over-all weight loss 34 percent.
	In vapor	Negligible loss.
	Partly immersed	Very severe attack; over-all weight loss 52 percent.
Commercial D, zircon type	In vapor *	2.1-percent weight loss.
	In vapor	6.7 percent weight loss.
BeO. (Abs. 0.02 percent)	Partly immersed	Original 0.5-in. diameter of immersed portion reduced by 0.008 in.
99 percent BeO, 1 percent MgO by weight. (Abs. 0.02 percent).	In vapor	Color change to 1-mm depth. Weight loss, 1.2 percent.
Do	Partly immersed	Discernible, but slight attack on immersed portion.
99 percent BeO, 1 percent CaO, by weight. (Abs. 0.01 percent.)	do	Only 0.007-in. decrease in diameter, but microscope shows interstitial penetration of PbO throughout specimen.
MgO; porous	do	0.02-in. decrease in diameter; PbO penetrated throughout mass, and isolated grains show considerable attack.
Al_2O_3, 99.95-percent purity. (Abs. 0.07 percent.)	Immersed	Considerable attack; over-all weight loss 9.8 percent.
ThO_2. (Abs. 1.9 percent)	In vapor	0.02-percent weight loss.
Chrysoberyl. (Abs. 0.03 percent)	do	No weighable weight loss.
Chrysoberyl. (Abs. 0.06 percent)	Partly immersed	Superficially no attack but microscope shows PbO penetration to about 0.06 in. depth and also interstitial solution products.
4MgO:96BeO:Al_2O_3 (mole). (Abs. av. 0.04 percent.)	In vapor	Duplicate samples showed 0.5-percent increase in weight. The microscope shows intercrystalline boundary attack to a depth of about 0.12 in.
MgO:16BeO:Al_2O_3 (mole). (Abs. 0.03 percent).	do	Showed 0.3-percent gain in weight.
MgO:16BeO:Al_2O_3 (mole). (Abs. 0.01 percent.)	Partly immersed	0.4 percent weight loss.

* Held for 4 hours at 1,000° C.

10. EFFECTS OF AUXILIARY OXIDES

This phase of the investigation was undertaken for two reasons: First, the addition of minor quantities of one or more oxides to a binary or ternary composition might lower the temperature range or enhance the degree of vitrification with no appreciable loss in mechani-

TABLE 15.—*Effect of minor oxide additions on the linear shrinkage (shr.) and absorption (abs.) of several compositions in the systems* BeO-Al_2O_3-ThO_2 *and* BeO-Al_2O_3-ZrO_2

[Duplicate tests were made only when the values of the first test appeared inconsistent with other values of a series. The asterisk (*) following an absorption value indicates that the specimen was overfired as judged by its deformation, blistering, or freezing to the platinum-rhodium plate on which it had been heated]

Oxide added	Matured at—	Base composition (mole)																	
		24BeO:Al_2O_3:ThO_2 [a]						96BeO: Al_2O_3: ThO_2 [a]						160BeO: 2Al_2O_3: ThO_2 [b]					
		Percentage by weight of oxide added to base composition																	
		8		4		2		8		4		2		8		4		2	
		Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.
	°C	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
CaO	1,600	16.0	1.00*	15.7	1.5	16.8	0.6			18.7	1.00*			19.8	0.01*	19.0	0.5*	18.4	0.02*
	1,550	12.8	0.01*	16.3	0.01*	18.4	.00			19.0	0.00			19.4	.01*	19.4	.01*	20.6	.02
	1,500	15.4	.01*	17.4	.01	18.7	.01			20.0	.00			20.3	.00*	20.0	.00	20.0	.00
	1,450	15.6	.02	17.3	.03	18.9	.06			19.4	.00			20.0	.02*	20.0	.00	21.1	.01
	1,400	16.5	3.3	15.9	4.5					19.5	.01			20.6	.02*	19.8	.01	20.2	.50
	1,350									19.2	.60			20.5	3.2	19.8	.04		
SrO	1,650			17.5	1.7														
	1,600			18.9	0.04														
	1,550			20.6	.01														
	1,500			19.7	1.14														
MgO	1,650			20.3	0.01														
	1,600			19.4	.02														
	1,550			19.8	.00											21.0	.32*		
	1,500			18.7	.19											21.9	.01		
	1,450			15.9	5.6											21.4	.01		
	1,400															19.8	.2		
	1,350																4.3		
SiO_2	1,700			18.7	0.00*	16.5	.01*			18.6	.01					18.9	0.00	18.9	.00
	1,650			17.4	.00	17.4	.01			18.4	.02			17.6	0.00*	19.8	.01	19.8	.38
	1,600	15.0	0.00*	17.0	.05	15.4	3.9			17.4	.29			17.9	.01	17.5	1.8	16.0	6.7
	1,550	16.7	1.13	14.9	5.9					11.6	12.4			14.3	7.8	14.7	9.1		
TiO_2	1,650	18.8	0.27*	18.2	0.01*	18.6	0.01*			21.6	0.01*	20.8	0.01*			21.3	0.01*	20.8	0.01*
	1,600	19.2	.62	18.9	.04	20.0	.06	20.3	0.00	21.3	.00	20.8	.01	20.6	0.03	21.1	.00	20.6	.00
	1,550	18.6	.97	19.8	.08	19.3	.54	20.6	.02	20.8	.06	20.6	.58	20.8	.01	20.6	.00	20.3	.60
	1,500	19.2	1.19	18.7	1.22	18.7	1.22	20.3	1.82	19.8	2.14	19.8	2.49	20.3	1.10	20.3	1.43	19.8	2.37

Oxide added	Matured at—	Base composition (mole)							
		48BeO:4Al_2O_3:ThO_2 [a]		48BeO:Al_2O_3:ZrO_2 [d]		24BeO:Al_2O_3:2ZrO_2 [d]		24BeO:2Al_2O_3:ZrO_2 [d]	
		Percentage by weight of oxide added to base composition							
		4		4		4		4	
		Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.
	°C	%	%	%	%	%	%	%	%
CaO	1,600	18.8	0.01*	18.8	0.01*	18.8	0.01*	18.8	0.01*
	1,550	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,500	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,450	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,400	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,350	19.2	.00	19.2	.00	19.2	.00	19.2	.00
SrO	1,650	19.2	0.00	19.2	0.00	19.2	0.00	19.2	0.00
	1,600	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,550	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,500	19.2	.00	19.2	.00	19.2	.00	19.2	.00
MgO	1,650	19.2	0.00	19.2	0.00	19.2	0.00	19.2	0.00
	1,600	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,550	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,500	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,450	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,400	19.2	.00	19.2	.00	19.2	.00	19.2	.00
SiO_2	1,650	19.2	0.00	19.2	0.00	19.2	0.00	19.2	0.00
	1,600	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,550	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,500	19.2	.00	19.2	.00	19.2	.00	19.2	.00
TiO_2	1,650	19.2	0.00	19.2	0.00	19.2	0.00	19.2	0.00
	1,600	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,550	19.2	.00	19.2	.00	19.2	.00	19.2	.00
	1,500	19.2	.00	19.2	.00	19.2	.00	19.2	.00

		48BeO:4Al$_2$O$_3$:ThO$_2$ [a]						48BeO:Al$_2$O$_3$:ZrO$_2$ [d]				24BeO:Al$_2$O$_3$:2ZrO$_2$ [d]				24BeO:2Al$_2$O$_3$:ZrO$_2$ [d]			
		Percentage by weight of oxide added to base composition																	
		8		4		2		4		2		4		2		4		2	
		Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
CaO	1,650											19.0	0.06[c]	18.1	0.02[c]	17.9	0.02[c]	16.8	0.00[c]
	1,600			16.5	1.9[c]	17.4	0.8	19.4	0.01	20.3	0.01	19.0	1.0	19.0	.04	18.4	1.1	18.1	.5
	1,550	12.6	4.0[c]	16.2	0.01[c]	18.2	.01	19.7	.01	20.8	.02	18.7	0.5	19.4	.07	18.1	1.3	18.7	.2
	1,500	16.7	0.02	18.1	.01	18.2	.01	19.8	.00	19.8	.03	18.7	.6	18.1	1.5	17.8	1.3	18.1	1.2
	1,450	16.2	.04	17.9	.06	18.2	.04	20.6	.02	20.6	.64								
	1,400	16.5	4.3	14.9	5.3			19.4	.35	19.0	3.13								
SrO	1,650							19.8	.08[c]	20.0	0.02[c]	17.9	1.7	18.7	1.0	19.4	0.2[c]	18.4	0.2[c]
	1,600							21.5	.6	21.5	.01	19.8	1.3	19.8	0.9	19.5	.9	19.5	.6
	1,550							21.6	.6	21.1	.04	20.0	0.9	20.0	.8	19.7	.5	19.2	.6
	1,500									22.2	.03								
	1,450									17.6	.62								
BaO	1,700							18.9	3.6[c]	20.0	.3[c]	17.9	3.4[c]	17.3	2.2[c]	18.2	1.5[c]	17.6	1.3[c]
	1,650							20.0	0.4	20.6	.1	19.0	1.3	19.0	1.2	18.9	0.9	18.4	0.8
	1,600							20.0	.4	20.8	.2	19.2	1.2	19.2	1.2	18.1	.8	18.7	.9
MgO	1,700							19.8	.6[c]	19.2	2.4[c]	17.4	3.0[c]	16.0	2.9[c]	16.0	3.5[c]	16.8	1.1[c]
	1,650							20.0	.00	19.5	0.2	18.9	0.8	18.9	0.9	17.6	1.0	18.2	0.7
	1,600							20.0	.01	20.0	.9	18.0	1.1	18.0	1.5	17.0	2.1	17.5	1.5
	1,550							21.3	.01										
	1,500							20.6	.00										
	1,450							19.8	.01										
	1,400							17.3	3.93										
SiO$_2$	1,700			17.9	0.00[c]	16.8	.00[c]	18.5	0.9[c]	18.7	.6[c]	18.1	1.6[c]	16.8	1.3[c]	17.9	1.3[c]	16.8	1.0[c]
	1,650			17.4	.00	17.1	.01	18.1	1.3	18.2	1.6	17.3	1.9	17.3	1.9	16.5	1.3	17.3	1.4
	1,600	15.2	0.00[c]	17.0	.06	16.5	2.8	17.1	3.1	14.9	7.0	16.8	2.5	15.5	4.2	16.3	2.1	16.0	3.6
	1,550	15.5	.05	14.4	6.4														
	1,500	15.6	2.6																
TiO$_2$	1,700							20.6	0.8[c]	20.0	0.4[c]	19.0	1.0[c]	17.6	0.9[c]	18.7	2.2[c]	17.4	1.0[c]
	1,650			19.2	0.02[c]	18.4	0.01[c]	20.0	.7[c]	20.0	.3[c]	18.1	1.0	18.4	.9	19.0	0.9	19.4	0.7
	1,600	18.9	0.03	18.6	.01	19.0	.00	21.1	.3	21.5	.04	19.8	1.1	20.1	1.4	19.8	1.0	20.0	.9
	1,550	18.5	.07	19.2	.10	19.2	.31	20.0	2.4	19.4	3.3	18.1	2.4	16.0	4.8	19.0	1.7	16.5	4.1
	1,500	18.9	.90	19.0	.85	18.4	1.52												

[a] Vitrified specimens of the base composition without oxide additions were obtained by heating at 1,650°, 1,700° C, and 1,750° C.
[b] Vitrified specimens of the base composition without oxide additions were obtained by heating at 1,600°, 1,650°, 1,700°, 1,750°, and 1,800° C.
[c] Vitrified specimens of the base composition without oxide additions were obtained by heating at 1,700° and 1,750° C.
[d] Vitrified specimens of the base composition without oxide additions were not obtained.

cal and electrical properties; and, second, as both the raw materials and production processes under plant conditions are apt to introduce extraneous oxides, it should be helpful if the manufacturer could estimate in advance what to expect from such additions. Accordingly, 2-, 4-, and 8-percent additions of PbO, CaO, SrO, BaO, MgO, B_2O_3, SiO_2, and TiO_2 were made to several bodies of the MgO-BeO-Al_2O_3, the BeO-Al_2O_3-ThO_2, and the BeO-Al_2O_3-ZrO_2 series. Values for linear shrinkage and for absorption are summarized in table 15 for those results believed to be of interest.

PbO was added only to compositions of the MgO-BeO-Al_2O_3 series. No values are presented for this series because there appeared to be little promise of improvement by means of the oxide additions, which included B_2O_3 and TiO_2 in addition to PbO.

(a) BeO-Al_2O_3-ThO_2 SERIES

Five compositions and additions of five oxides were investigated in this series, although each of the five oxides was not added to each of the base compositions. Additions of 4 percent of CaO, of MgO, or of SiO_2 to the mole composition BeO:Al_2O_3:2ThO_2 produced no useful specimens, and the data are therefore not presented. The summary of results for the other four compositions (table 15) shows that some of the additions effected an appreciable lowering of the vitrification range, and the addition of 2 or 4 percent of CaO also widened this range for the 96:1:1 and 48:4:1 compositions. In general, 4-percent additions were the most beneficial. Specimens containing CaO were grayish in color, and a tendency to produce a low viscosity glass that segregated in the lower portions of a specimen increased wish increase in CaO. For example, no satisfactory test pieces were obtained with the 160:2:1 composition containing 8 percent of CaO, but a 2-percent addition of CaO to this base composition, and heating at 1,500°, produced bodies of good texture and with an average strength in compression of 188,000 lb/in^2. The same base composition with no additions, and heated at 1,725° C., had an average strength of 244,000 lb/in^2. With a 4-percent addition of MgO, vitrification was obtained at 1,500° and 1,550° C. Four-percent additions of SrO or MgO to the composition 24BeO:Al_2O_3:ThO_2 produced good specimens at 1,550° and 1,600° C.

Additions of SiO_2, with the possible exception of 4-percent additions to the 48:4:1 and 24:1:1 compositions, were not beneficial. The color of specimens containing TiO_2 was generally some shade of buff. The 8-percent addition to 24BeO:Al_2O_3:ThO_2 was definitely harmful, but 8 percent added to the other three bodies, and 2- or 4-percent additions to all of the four bodies (table 15) lowered the minimum vitrifying temperature to 1,550° C., and the range is from 1,550° to 1,600° C. Three specimens of 160BeO:2Al_2O_3:TbO_2 with an addition of 2 percent of TiO_2, and heated at 1,550°, had an average strength in compression of 250,000 lb/in^2.

Electrical resistivity and relative thermal conductivity values for specimens of composition 24BeO:Al_2O_3:ThO_2 are given in table 16. The values indicate an appreciable increase in electrical resistance by 4-percent additions of CaO, SrO, or MgO and a decrease by additions of SiO_2 and TiO_2. The 4-percent addition of MgO increased the thermal conductivity slightly, and the other oxide additions lowered it about 50 percent.

(b) BeO-Al_2O_3-ZrO_2 SERIES

As stated previously, only one of the compositions investigated in this system ($48BeO:Al_2O_3:ZrO_2$) even approached vitrification when no auxiliary fluxes were used. It is evident from the values in table 15 that oxide additions to three compositions resulted in some improvement. Two percent of CaO in $24BeO:Al_2O_3:2ZrO_2$ produced vitreous specimens at 1,550° and 1,600° C. Both 2- and 4-percent of CaO, and 2 percent of SrO, in composition $48BeO:Al_2O_3:ZrO_2$ produced satisfactory vitrification ranges. In this same composition, 2 percent of TiO_2 was helpful, but the effect of 4 percent of MgO was the most pronounced in lowering and lengthening the vitrification range. The color of all the specimens was some shade of buff or ivory.

It was noticeable, in handling the vitreous specimens of this system, that they are much more resistant to chipping, and to mechanical shock generally, than is true of the bodies containing ThO_2. Their resistance to crushing also is good as shown by the following values:

$24BeO:Al_2O_3:2ZrO_2$ +2% CaO (matured at 1,575° C.)..... 249,000 lb/in².
$48BeO:Al_2O_3:ZrO_2$ +2% CaO (matured at 1,550° C.)..... 251,000 lb/in².
$48BeO:Al_2O_3:ZrO_2$ +4% MgO (matured at 1,625° C.)..... 275,000 lb/in².

TABLE 16.—*Electrical resistivity (T_e) and relative thermal conductivity values showing effect on these properties of minor oxide additions to compositions in the* BeO-Al_2O_3-ThO_2 *and* BeO-Al_2O_3-ZrO_2 *systems (each value represents 1 specimen)*

Specimen from test No.	Base composition (mole)			Oxide added	Matured at—	Absorption	Electrical resistivity (T_e value)[a]	Thermal conductivity[b]
	BeO	Al_2O_3	ThO_2					
					°C	%	°C	
233-L	24	1	1	None	1,650	0.01	945	
300-L	24	1	1	do	1,750	.02		11
248-L	24	1	1	4% CaO	1,500	.01	1,025	
252-L	24	1	1	do	1,550	.01		6
250-L	24	1	1	4% SrO	1,600	.00	1,100	
269-L	24	1	1	do	1,550	.01		6
256-L	24	1	1	4% MgO	1,550	.00	1,045	
281-L	24	1	1	do	1,600	.02		14
247-L	24	1	1	4% SiO_2	1,650	.00	775	
250-L	24	1	1	do	1,600	.05		5
255-L	24	1	1	4% TiO_2	1,650	.01	735	
241-L	24	1	1	do	1,600	.04		5
	BeO	Al_2O_3	ZrO_2					
164-L	48	1	1	None	1,750	.42	1,055	10
229-L	48	1	1	4% CaO	1,500	.00	1,065	8
233-L	48	1	1	4% SrO	1,650	.06	990	11
279-L	48	1	1	8% MgO	1,450	.01		33
286-L	48	1	1	do	1,550	.00	858	
205-L	48	1	1	2% TiO_2	1,700	.42	755	14

[a] The T_e value for electrical resistivity is the temperature at which, by calculation based on test values, a 1-cm cube of the material has a resistance of 1 megohm. The values were determined by E. N. Bunting.
[b] The thermal-conductivity value is the reciprocal, multiplied by 100, of the temperature drop through a 0.5-in. height of specimen approximately ½ in. in diameter and resting on a hot plate at about 250° C. The values were determined by E. N. Bunting.

An exploratory series of tests, made by substituting MgO, CaO, or SiO_2 for the BeO in $6BeO:Al_2O_3:5ZrO_2$ and $BeO:Al_2O_3:2ZrO_2$, did not produce vitrification. The same comment applies to trials in which 4 percent of the oxides mentioned was added to these composi-

tions. As no data of value were obtained, they are not tabulated.

The values in table 16 indicate that SrO, MgO, and TiO_2 additions to bodies of this series would lower the electrical resistance and that MgO would increase the thermal conductance. Otherwise, the additions had no significant effect.

V. SUMMARY

In order to supply fundamental information upon which to base the practical development of new ceramic compositions for service conditions of increased severity, there was undertaken a study of the characteristics of variously heated oxides in simple binary and ternary combinations. The oxides used in these simple combinations were MgO, CaO, BaO, BeO, Al_2O_3, ThO_2, and ZrO_2. The investigation included the study of phase relations as well as the fabrication and testing of specimens for mechanical and electrical tests, and for other properties having a bearing on their usefulness. The work was supplemented by a limited study of the effects of minor additions of CaO, SrO, BaO, B_2O_3, SiO_2, TiO_2, or PbO. The materials were of the highest purity obtainable commercially. Temperatures ranging from about 1,450° to over 1,900° C. were obtained in an especially designed furnace heated electrically with ThO_2-Y_2O_3 resistors.

In the system BeO-Al_2O_3, large crystals, and also vitrified specimens, of chrysoberyl (BeO.Al_2O_3) were obtained readily. Two eutectics, one at 1,880° C. and 14 wt. percent of BeO, and one at 1,865° C. and 26.9 wt. percent of BeO, were indicated. The electrical resistance of chrysoberyl was very good (T_e=1,285° C.), but the strength in compression and thermal conductivity were only fair. The linear thermal expansion was 0.788 percent between room temperature and 1,000° C. Tests were made also on specimens of BeO and of Al_2O_3 containing small but differing amounts of impurities.

In the system MgO-BeO a simple eutectic was indicated at 1,855°C and 48.2 wt percent of BeO. Compositions containing not less than about 79 wt percent of BeO could be vitrified. Strength in compression was fairly high, electrical resistivity was very good, and the thermal conductivity of bodies containing not more than about 29 wt percent of MgO was practically equal to that of pure BeO.

In the system MgO-Al_2O_3, a limited number of tests were made on the compound $MgAl_2O_4$ (spinel). It was noted that heating at 1,650° was sufficient for an 80- to 90-percent conversion of a MgO-Al_2O_3 mixture to spinel, and specimens heated at 1,900° C were not completely vitreous. The T_e value for spinel was 1,170° C, and the thermal conductivity value was 1.9.

Approximate fields of stability were established for the system MgO-BeO-Al_2O_3, including a small field near the Al_2O_3 apex for what is believed to be a ternary compound. The lowest fusing eutectic, having the composition (by weight) 44.4 percent of MgO, 27.5 percent of BeO, and 28.1 percent of Al_2O_3 (4MgO:4BeO:Al_2O_3, mole ratio), fused at 1,640° C. A considerable range of compositions could be formed into vitreous specimens of which many, particularly those in the high BeO area, had high resistance to crushing, good dielectric properties, and high electrical resistivity, as well as high thermal conductivity. For example, specimens of mole composition MgO:24BeO:Al_2O_3 had an average strength in compression of 286,000 lb/in.^{2}, a

dielectric constant (K value) of 6.9, and a power-loss factor of 0.06 percent. The T_e value ranged from 1,137 to 1,210, and the average thermal conductivity value was 10.

In the CaO-BeO-Al_2O_3 system, the eutectic in the subordinate system CaO-BeO was found at 1,405° C and approximately 65 wt percent of CaO. In general, the "vitrification surface" is about 100 deg C lower than for the MgO-BeO-Al_2O_3 system, but the test pieces were coarsely crystalline, and none was prepared for test.

The system BaO-BeO was investigated only superficially. No specimens for mechanical or electrical tests were prepared. The thermal reactions may be complicated by a low-temperature eutectic between BaO and $BaCO_3$.

The system BeO-Al_2O_3-ThO_2 is distinctively one of high temperatures. The eutectic in the Al_2O_3-ThO_2 system occurs at 1,910° C and 60.7 wt percent of Al_2O_3, and the lowest fusing ternary eutectic was found at 1,795° C, and probably is near the mole composition $4BeO:2Al_2O_3:ThO_2$. The optimum temperature interval for producing vitreous specimens lies between 1,600° and 1,750° C. For mole compositions $160BeO:2Al_2O_3:ThO_2$ and $48BeO:Al_2O_3:ThO_2$, average strengths in compression were, respectively, 244,000 and 279,000 lb/in^2. Power-loss values were less than 0.01 percent, and the dielectric constant ranged from 7 to 8.

The BeO-Al_2O_3-ZrO_2 system resembles the BeO-Al_2O_3-ThO_2 system as regards phase relations, but the beginning of fusion of corresponding ternary mixtures will average about 50 deg C lower. Fusion for the Al_2O_3-ZrO_2 eutectic was observed at 1,885° C and the composition, by weight, was 55 percent of ZrO_2 and 45 percent of Al_2O_3. The lowest ternary eutectic is indicated to be at about 1,750° C and the mole composition $2BeO:Al_2O_3:ZrO_2$. The nearest approach to vitrification was obtained with the mole composition $48BeO:Al_2O_3:ZrO_2$, which had an average absorption of about 0.4 percent when heated at 1,750° C. No specimens were prepared for mechanical or electrical tests.

Tests for determining relative resistance to attack by PbO liquid and vapor indicate (a) that attack by the liquid on immersed test pieces is much greater than by the vapor on pieces supported above the liquid, (b) that attack at 1,100° C is much greater than at 1,000° C, and (c) that siliceous bodies were the least, and "high BeO" bodies the most, resistant to attack.

Additions up to 8 percent of an auxiliary oxide, such as PbO, CaO, SrO, BaO, MgO, B_2O_3, SiO_2, or TiO_2, did not improve significantly the vitrification behavior of compositions in the system MgO-BeO-Al_2O_3. In the system BeO-Al_2O_3-ZrO_2, additions of CaO or MgO were the most effective in producing vitreous specimens, but the composition range was very limited. Auxiliary oxide additions to four compositions in the BeO-Al_2O_3-ThO_2 system effected a lowering of at least 50 deg C in the minimum vitrification temperature in most cases. CaO in 4-percent additions was the most beneficial and, for one composition ($160BeO:2Al_2O_3:ThO_2$), vitreous pieces were obtained at 1,350° C. Specimens of this composition with an addition of 2 percent of TiO_2 had an average strength in compression of 250,000 $lb/in.^2$. Four-percent additions of CaO, SrO, or MgO increased the electrical resistance of the mole composition $24BeO:Al_2O_3:ThO_2$, but SiO_2 or TiO_2 additions lowered it. The 4-percent addition of MgO increased

the thermal conductivity slightly, but the other oxide additions lowered the conductivity about 50 percent.

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ANALYSIS OF A STANDARD SAMPLE OF THE CARBURETTED WATER-GAS TYPE BY LABORATORIES COOPERATING WITH THE AMERICAN SOCIETY FOR TESTING MATERIALS

By Martin Shepherd

ABSTRACT

This is a report of the analysis of a standard sample of carburetted water-gas by 24 laboratories in cooperation with Subcommittee VII of Committee D–3 of the American Society for Testing Materials. The data are presented in a series of frequency distribution plots, which show at a glance how the analyses compare with respect to each component of the gas mixture, as well as the calculated heating value and specific gravity. These plots form a clear picture of this type of gas analysis in this country. Although some very creditable work was reported, the need for some standardization is evident.

CONTENTS

	Page
I. Task of Committee ASTM D–3–VII on the analysis of gaseous fuels	314
II. Cooperating laboratories	314
III. Preparation of standard gas sample ASTM D–3–VII–1	315
IV. Other instructions and information furnished with the standard sample	317
V. Volumetric reproducibility of the analytical apparatus used by the cooperating laboratories	318
VI. Apparatus and methods used for the analysis of standard gas sample ASTM D–3–VII–1	321
1. Apparatus	321
2. Methods of analysis	322
VII. Results of the cooperative analysis of the standard gas sample ASTM D–3–VII–1	323
1. Manner of presenting the analytical data	323
2. Specific gravity calculated from the analyses compared with the known specific gravity	324
3. Calculated heating value compared with measured heating value	327
4. Comparison of laboratories	330
5. Carbon dioxide	330
6. Oxygen	331
7. Ethylene	332
8. Carbon monoxide	333
9. Hydrogen	334
10. Methane and ethane	336
11. Nitrogen	336
12. All constituents	336
VIII. Conclusions	337
IX. Addenda. A comparison of results obtained by the mass spectrometer with analyses by the conventional volumetric methods of absorption and combustion	338

I. TASK OF COMMITTEE ASTM D-3-VII ON THE ANALYSIS OF GASEOUS FUELS

Subcommittee VII of Committee D-3 of the American Society for Testing Materials has been assigned the task of standardizing the analysis of gaseous fuels. The Subcommittee is approaching this task with certain reservations derived from an acquaintance with gas-analysis methods, gas-analysis apparatus, and gas analysts. The reason for such reservations usually become apparent when a gas analyst is asked to substitute a new reagent, pipette, procedure, method—or a whole new apparatus or system of analysis—for one that he has been using satisfactorily. Such a request is unamiable and might very often be unreasonable. Indeed, if it can be demonstrated by actual measurement that an apparatus or method now in use will give satisfactory results, there is no real justification for insisting that it be discarded in favor of another which may be sponsored as the official instrument of some group.

Since it seems reasonable and fair to approve as standard any apparatus and method capable of giving satisfactory analytical results, it remains only to decide what are satisfactory analytical results, and which methods and apparatus will yield these results. To reach these decisions, two steps are being taken.

First, the various purposes to be served by the analytical data are listed, and the necessary accuracy with which each component of each type of fuel gas must be known in order to serve each specific purpose is then estimated. These estimates afford the first criterion by means of which the suitability of analytical methods and apparatus may be judged, but they are subject to revision when more is known about the limiting attainable accuracies of the analytical methods, and also when the significance of the term "necessary" in the phrase "necessary accuracy" has been evaluated with more realism than enthusiasm.

Second, the accuracy and reproducibility of existing apparatus and methods are being measured by the direct procedure of a series of cooperative analyses of standard gas samples of various types. (Although these samples are being prepared at the National Bureau of Standards, they are not to be confused with the Bureau's series of Standard Samples available for purchase. These gas samples are being prepared for free distribution to laboratories cooperating with ASTM Committee D-3 in this project.)

The analytical results obtained so far from the examination of these standard samples represent our first clear picture of gas analysis in this country.

This paper reports the results of the analysis of the first standard sample of a planned series. The sample is of the carburetted water-gas type for analysis by the conventional volumetric absorption and combustion methods.

II. COOPERATING LABORATORIES

Cooperating laboratories include those of State and Federal agencies and of colleges, but the greatest contribution has come from the laboratories of the gas, petroleum, and steel industries. The laboratories are located throughout the United States. They are equipped with many types of apparatus, mostly modern, and employ different analytical methods. These methods and apparatus will be noted

with the presentation of the analytical data. Taken as a whole, the work represents the best present-day American practice.

Of the 24 laboratories that analyzed the carburetted water-gas sample, all but one (a college) employed chemists specifically trained in gas analysis. One laboratory used high-school talent, 1 used high-school and college graduates, 17 used college graduates, and 5 answered "yes" to the question, "Do these men (gas analysts) have the equivalent of high-school or college education?" Nineteen of the laboratories did gas analysis regularly and 5 (mostly colleges) intermittently.

Most of the cooperating laboratories preferred anonymity, and the names of all are accordingly withheld from publication. This has the advantage of placing the results on an impersonal basis, which removes any inhibition to the open expression of constructive criticism and provides no stimulus for an unamiable discussion of results. It does deprive one of the chance to appraise the likely worth of results from a laboratory whose equipment, personnel, and operation are well known from personal observation. Appraisal based on this sort of acquaintance is of real value in a good practical sense, but is not an actual requisite in a cooperative study of this sort. Anonymity is also a pseudonym for modesty in this instance, for it has deprived many of the laboratories of taking credit for really fine work.

III. PREPARATION OF STANDARD GAS SAMPLE ASTM D-3-VII-1

Standard Sample ASTM D-3-VII-1, carburetted water-gas type, was prepared to conform with the range of composition at present accepted by Subcommittee VII, which is

	Percentage by volume
CO_2	6 to 1
O_2	1 to 0.2
N_2	10 to 2
"Illuminants"	15 to 5
H_2	45 to 30
CO	40 to 30
CH_4	17 to 5
C_2H_6+	3 to 2

The sample was made up from the following compressed gases obtained from commercial sources:

Type of gas	Approximate purity	Chief impurity
	Percent	
CO_2	99.9	Air
O_2	99.7	N_2
N_2	99.5	O_2
C_2H_4	99.5	Homologues
H_2	99.7	O_2
CO	99.7	H_2
CH_4	99	N_2 and C_2H_6+
C_2H_6	98	C_2H_4 and C_3H_8

As this sample was not prepared from gases of known high purity, its actual composition was not known. Its heating value and specific gravity were carefully measured. The sample, therefore, serves three definite purposes, as it will establish (1) reproducibility,[1] (2) ability to compute correct heating value, and (3) ability to compute correct specific gravity. It will not serve as a final criterion of *accuracy*,[1] except in respect to the computation of heating value and specific gravity, as the composition was not predetermined.

The sample was prepared under a pressure of 350 psi in the large storage and mixing tank used to prepare the mixtures for the Bureau's study of specific-gravity instruments.[2] After very thorough mechanical mixing, the uniformity of the sample was definitely established by sampling from various parts of the tank and measuring any difference in composition by means of a 1-m Zeiss gas interferometer. The sample was then transferred to small sample cylinders as follows:

1. The sample cylinders, equipped with needle valves having vacuum-tight packing, were connected to a single welded manifold by means of high-pressure unions. The large mixing tank and a vacuum pump were connected to this same manifold. The whole system, including the manifold and opened sampling cylinders, was evacuated to 0.0001 mm Hg pressure overnight. Thereafter, with vacuum pump disconnected, the increase of pressure within the whole system was less than 0.0001 mm during the first hour. Much less than 1 hour was required to transfer the gas sample from the mixing tank to the sample cylinders. Contamination from leakage was, therefore, quite insignificant.

2. The small cylinders were flushed with the sample from the mixing tank by alternate filling to 2 atm and evacuating to 1 mm Hg. After the third flushing, the sample cylinders were filled to 320 psi. With full pressure on the manifold, the sample cylinders were then closed. The manifold was then opened to a water seal, and no leakage from the cylinders was observed overnight.

3. All the sample cylinders issued for the cooperative analysis of this sample were thus filled simultaneously from the manifold connected to the single, uniform source of supply. The samples were, therefore, identical at the date of issue.

The sample was issued in February 1940. During March, April, May, and June, 18 of the 24 cooperating laboratories reported, and of the remaining 6 laboratories, 4 reported in July, 1 in August, and 1 in September. As the sample contained carbon monoxide under pressure in steel, the question of a significant change in composition because of the formation of iron carbonyl has been raised. Although this reaction no doubt occurred to some slight extent, it apparently did not alter the composition of the sample by any significant amount. During the first 4 months, when most of the analyses were performed, the measurements of specific gravity indicated a lowering of 0.0002. This corresponds to approximately 0.04 percent by volume of carbon monoxide. In 4 years' time, the measured heating value of the gas, still stored under pressure in steel, was 0.8 Btu lower than indicated

[1] Lest there be any confusion as to the meaning of the terms "accuracy" and "reproducibility," it should be stated that the conventional concepts are here implied. Accuracy is measured in terms of agreement with a true value; reproducibility is measured in terms of the mutual agreement of a series of measurements of the same property of a substance. As a matter of convenience, reproducibility has long served the gas analyst in lieu of a definite measurement of accuracy. Eventually this situation will be corrected.

[2] F. A. Smith, J. H. Eiseman, and E. C. Creitz, Tests of instruments for the determination, indication, or recording of the specific gravities of gases, Misc. Pub. NBS M177. [Publication pending.]

by the original measurement. This is in the wrong direction to be accounted for by loss of carbon monoxide. A loss of 1 percent of carbon monoxide would have raised the heating value of this sample 3 Btu. Finally, the analyses from March to September show no significant trend, down or up, with respect to the carbon monoxide found.

It is accordingly entirely reasonable to assume that identical samples were analyzed in all the laboratories, provided the samples were introduced into the apparatus for analysis without contamination.

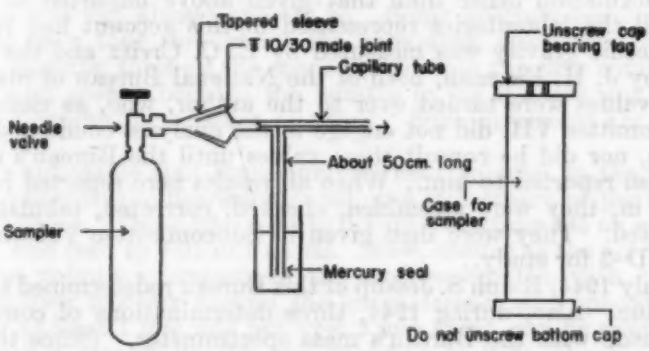
To avoid contamination while transferring the sample to the burette the following illustrated instructions for a definite procedure were furnished the laboratories.

INSTRUCTIONS REGARDING SAMPLER AND SAMPLING

1. The cylinder containing the sample is shipped in a metal case made from standard pipe fittings. Save this for return of the cylinder, which must be returned immediately upon completion of your analyses.

2. The cylinder is equipped with a very special vacuum-type needle valve. DO NOT close this valve with anything but the thumb and one finger. DO NOT force the valve shut. If too much twist is applied to the valve handle, the seat will be ruined.

3. Remove the dust cap from the valve and attach the sampling fitting, which terminates in a thin brass tapered sleeve. This sleeve fits a standard glass interchangeable joint, male part, size ⅝ 10/30. This glass joint should be sealed to the brass sleeve by a thermoplastic cement of the DeKhotinsky type, or other cement capable of making a gas-tight joint. We find the arrangement sketched below desirable.



With cock of burette closed, gently open needle valve until gas bubbles out through mercury seal. When this line is flushed, take gas into burette and discard until horizontal portion of sampling line is flushed. About 50 ml in all is adequate for flushing capillary lines. Leave connected to burette for next sample to be taken. Use mercury seal as manometer to avoid sampling under reduced pressure. If direct glass seal or interchangeable joint is not used in connecting to burette, flush sampling line each time with about 20 ml of gas. For convenience and safety, we prefer interchangeable joints secured with DeKhotinsky or a heavy lubricant.

IV. OTHER INSTRUCTIONS AND INFORMATION FURNISHED WITH THE STANDARD SAMPLE

In addition to the sampling instructions, these general instructions were issued.

INSTRUCTIONS REGARDING ANALYSIS AND RECORDING OF DATA

(1) The sampler should yield about 6 liters of gas, an amount adequate for flushing, saturating the reagents, and a good many analyses. Make at least 10 analyses. If possible, several analysts should each perform a group of 10 determinations.

(2) Report the data completely, including all burette readings, formulae used in computation, and relevant notes. Tabulate these data on a single sheet of paper.

(3) Furnish a photograph of the apparatus used at the time these analyses are performed. The committee desires this.

(4) For the sake of uniformity, compute the heating values from table 14 given on page 38 of NBS Circular C417, Calorimeter Tables, considering "Illuminants" as ethylene. If you wish to take exception to these values, state this and compute a second heating value as you wish.

(5) For the sake of uniformity, compute densities from the table given on page 3, volume 3, International Critical Tables.

(6) If you have not already given a description of the analytical apparatus used, include this. If a standard model, give name and cite reference. Note any modifications of your own.

In addition to these instructions, the following information was furnished with each sample.

(1) The *range* of composition as previously noted, with a list of the gases used to prepare the sample, also previously given.

(2) The range of heating value was expressed as 500 to 600 Btu per ft.[3]

(3) A brief description of the preparation of the sample to show the cooperating laboratories that each one received the same sample.

In no case did any analyst who made any of these determinations have any other knowledge of the properties of this sample, nor was any information other than that given above imparted to anyone until all the laboratories represented in this account had reported. The specific gravity was measured by E. C. Creitz and the heating value by J. H. Eiseman, both of the National Bureau of Standards. These values were turned over to the author, who, as chairman of Subcommittee VII, did not engage in the analyses conducted at this Bureau, nor did he consult these values until the Bureau's analyses had been reported to him. When all results here reported had been turned in, they were assembled, checked, corrected, tabulated, and illustrated. They were then given to Subcommittee VII and Committee D–3 for study.

In July 1944, Ralph S. Jessup of this Bureau redetermined the heating value. Also, during 1944, three determinations of composition were made with the Bureau's mass spectrometer. (Since the cooperative analyses had been reported, the 1944 measurements could have been made with a knowledge of the results previously obtained. Actually, no reference was made to previous results, with the single exception of the final analyses by the mass spectrometer.)

V. VOLUMETRIC REPRODUCIBILITY OF THE ANALYTICAL APPARATUS USED BY THE COOPERATING LABORATORIES

As we are dealing here with a volumetric analysis, the accuracy is fundamentally limited by the measurement of the gas volumes involved during the course of an analysis—and this is so obvious that it is often forgotten. Just to make sure that everything was in order before the standard sample was analyzed, and also to evaluate the

volumetric system (including its operator), each laboratory was asked to perform a series of simple measurements. The instructions are here reproduced.

VOLUMETRIC REPRODUCIBILITY OF APPARATUS

In addition to obtaining the analytical data, make the following measurements, using air as the gas to be measured. These measurements can well precede the analyses.

(1) Take approximately 90 ml of air into the burette, balance the pressure, and read the volume. Destroy balance, rebalance, and read again. Make and record 10 such measurements. Note temperature of water jacket.

(2) Now raise the temperature of the water in water jacket 2 degrees centigrade, and repeat measurements as made above.

(3) and (4) Repeat (1) and (2) with approximately 30 ml of air in the burette.

(5) Take three successive portions of about 30 ml of air, measure each and transfer to combustion pipette, then return and measure combined volume of the three portions. Repeat this procedure three times. Record all data.

(6) Measure approximately 50 ml of air in burette. Now place burette and distributor and manometer under a reduced pressure which will not quite upset manometer, allow to stand thus 10 minutes, rebalance and read volume.

(7) Repeat (6), but place under positive pressure. If (6) or (7) shows presence of leaks, locate and repair before proceeding with analyses.

These simple measurements proved to be of no significance to some laboratories, but were of real interest to others. Several faulty burettes, supposedly calibrated, were discovered and actually calibrated. Some analysts who had presumed that 30 ml+30 ml+30 ml, measured separately, would always equal a measured 90 ml found that this was not always exactly so. Some analysts conducted an inert gas on a tour throughout the apparatus, wandering over the various reagents, through the copper oxide, into the slow combustion pipette, and always back to the burette to see if there was loss or gain, or a comforting absence of either. Such diversions are always profitable.

It was noticeable that some analysts read volumes to the nearest 0.1 ml, others to the nearest 0.05 ml, and still others to the nearest 0.01 or 0.02 ml. Those who read to 0.1 ml sometimes lift an eyebrow at those who read to 0.01 or 0.02 ml. Now, insofar as the actual estimation of volume is concerned, the modern burette, with all lines engraved over halfway around the circumference and spaced longitudinally at least 1 mm and not over 2 mm apart, can be read rather easily with a reproducibility corresponding to 0.02 ml. The usual burette is marked in intervals of 0.2 ml, and the lines bounding this interval are about 1.2 to 1.5 mm apart. There are numerous instances in many laboratories where tenths of a millimeter are independently estimated by different observers with excellent agreement. This case is no exception, and this has been demonstrated by many years of independent observation with various observers checking one another. It has also been demonstrated by moving a chromium-plated rod, shaped to correspond to a mercury meniscus, within a tube, graduated to correspond to a gas analysis burette, and checking the estimated portion of the rod with its actual position measured by means of a micrometer head. It is true that errors induced by faulty temperature-pressure compensation and saturation may be greater than the

0.02 ml estimated in reading the burette, but this is no real argument against getting what is readily available from the burette.

The fact that three standards of reading were employed makes a comparison of the prescribed volumetric measurements rather difficult, as it is possible that where no deviation was noted on any test, an actual deviation was within the limit of 0.1 ml, and conversely where deviations of 0.1 ml are reported, they may actually have been somewhat less. The data have been condensed and are tabulated in table 1. The first column gives the laboratory number. The next four columns give the average change in volume noted in tests 1 to 4, inclusive, previously noted. The succeeding columns give the differences in volumes noted during test 5, and the average of these differences. This last average is the arbitrary volumetric reproducibility noted in the tables of analytical results to follow.

TABLE 1.—*Measurement of volumetric reproducibility and accuracy of all apparatus used*

Lab. No.	Test number										Average of test 5
	1	2	3	4	5						
	ml	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*
1	0	0	0	0	0.2	0.1	0.2				0.17
2	0	0	0	0	.06	.03	.04	0.03	0.03		.04
3	0	0.54±.17	(a)	(a)	.1	.1	.1	.4	.1	0.2	.17
4	0	0	0	0	.9	.6	.5				.7
5	.01	0.01	.01 to .02	.01	.03	.02	.06				.04
6	0	0	0	0	0	0	.05				.02
7	.01	0	0	0	.05	.05	.05				.05
8	.02	0.02	0.04	.02	.1	.2	0				.1
9	.04	0.03	0	.01	.2	.2	.3				.23
10	.02	0.02	0	.03	.2	.2	.1				.17
11	.01	0.02	0.01	.01	.02	0	0				.01
12	.05	0.05	0.05	.05	.1	0	.05				.05
13	0	0	0	0	0	0	0				0
14	.02	0.02	0.02	.02	(b)	(b)					
15	0	0	0	0	0	0	0				0
16			(a)	(a)							
17	0	0.01	0	0	.05	.05	0				.03
18	.02	0	0	.03	0	0	0				0
19	.02	0.02	0.02	.01	.1	.1	.1				.1
20			(a)	(a)							
21	.01	0	0	0	0	.01	.08				.03
22	0	0	0	0	.2	.1	0				.1
23	.01	0	0	0	.4	.25	.2				.3
24	.02	0.02	0.02	.02	.02	.02	.02				.02

[a] Not done.
[b] Incomplete.

Tests 1 and 3 were simple measures of volumetric reproducibility as it might be affected by the manometric system and the ability of the analyst to adjust pressures and read volumes. This test also measures the ability of the apparatus to maintain the meniscus of the confining liquid within the burette in the fixed position corresponding to the proper pressure balance until the volume is determined. This becomes important when there is no stopcock to arrest the flow of confining fluid between burette and leveling bulb, especially when the analyst must hold the leveling bulb while reading the volume—no task for a nervous man. A glance at the tabulated data shows no differences greater than 0.05 ml and average reproducibility of about 0.02 ml.

Tests 2 and 4 measured the volumetric reproducibility as it might be affected by a change of temperature and a corresponding change in equilibrium in the pressure-temperature compensation. The conventional pressure-temperature compensator was part of the regular equipment of most of the apparatus used. This device is certainly one of the most convenient bestowed upon gas analysts, and the greatness of its convenience has dulled curiosity concerning its behavior. It is essentially a differential gas- and vapor-pressure thermometer, and it can be reasonably expected to react accordingly with respect to changing temperature. If the degree of this reaction is the same in burette and compensating tube, all is well. But uniformity of temperature within the water jacket and rate of heat transfer into the burette and compensator may not always be favorable, particularly as regards saturation with respect to water vapor in the compensator with a rising temperature. It is accordingly comforting to note no change in apparent volume greater than 0.05 ml, with an average of about 0.02 ml, reported from tests 2 and 4. There is one exception. Laboratory 3 reported fairly large changes of volume with rising temperature. The apparatus involved was not equipped with a pressure-temperature compensator, so that such an effect was to be expected. However, the average change was 0.54 ± 0.17 ml per degree centigrade for an average volume of 76.4 ml; the expected change in the temperature range existing was 0.40 ml per degree centigrade; the reproductibility (± 0.17) is not too comforting.

Test 5 is a measurement of volumetric accuracy, and illustrates that the total volume may not equal the sum of its parts as actually measured. The data rather speak for themselves, although the fact that some series of readings were made to the nearest 0.1 and others to the nearest 0.01 precludes any close comparisons. This simple test was the means of discovering several burettes that were in error by really significant amounts, although they were presumably calibrated instruments.

In no case were leaks discovered and reported during tests 6 and 7. We can then assume that the apparatus used, insofar as the measurement of volumes is concerned, was free from leakage.

VI. APPARATUS AND METHODS USED FOR THE ANALYSIS OF STANDARD GAS SAMPLE ASTM D-3-VII-1

1. APPARATUS

It has been stated that most of the analytical apparatus used in this cooperative investigation was of the modern type. The apparatus may be classified with respect to the system of volume measurement, the arrangement of pipettes or reaction tubes, and the confining fluid. For convenience, a set of abbreviations is used.

V_1—Volumes are made comparable by means of a pressure-temperature compensator with manometer interposed between the compensating tube and the burette.

V_2—Pressure within the burette is balanced against existing barometric pressure, and gas volumes are corrected from the observed pressure and temperature to a common basis, including a correction for changes in the saturation pressure of water.

V_3—Pressure in burette is balanced against atmospheric pressure, but no correction is made for changes in pressure or temperature during analysis.

V_4—Volumes are measured by observing the pressure exerted within a constant volume.

R_1—Pipettes are connected to the burette by a manifold.

R_2—A single pipette, connected to the burette, serves for all reactions.

R_3—Pipettes are temporarily connected in succession to the burette as the different reactions are progressively conducted.

R_4—The burette itself serves as a reaction tube.

Hg—Mercury is used as the confining fluid.

H_2O (with appropriate subscript)—An aqueous solution serves as the confining fluid.

Thus the abbreviation V_1R_1Hg designates an apparatus equipped with pressure-temperature compensator and manometer, manifold connecting pipettes to burette, with mercury serving as the confining fluid. Twenty of the twenty-four laboratories used this type of apparatus. One laboratory used this type with acidified water as the confining fluid. One used a Bone and Wheeler apparatus, which is widely employed in Great Britain. This would be abbreviated V_4R_2Hg, as it is equipped with a constant volume burette and one permanently connected pipette. It is not as convenient to use as the models more favored in America, but does greatly reduce the errors caused by physical-solubility of gases in the various reagents. One laboratory used an apparatus without compensator, but with manifold to connect pipettes (V_2R_1Hg). And finally, one laboratory used a Hempel apparatus (V_2R_3Hg).

Photographs of all the apparatus actually used were requested, and 18 were submitted. These are not reproduced in this paper, but are on file if needed. In general, they show that modern apparatus in good condition was used.

2. METHODS OF ANALYSIS

When all the reports were assembled, it was evident that three major methods of analysis had been used. For abbreviation and identification in the figures, they are designated by roman numerals and are outlined below.

Method I:

Carbon dioxide was determined by absorption in a solution of potassium or sodium hydroxide.

Ethylene ("Illuminants") was determined by absorption in fuming sulfuric acid or bromine.

Oxygen was determined by absorption in a solution of potassium pyrogallol or in a chromous solution.

Carbon monoxide was determined by absorption in solutions of cuprous chloride (in various modifications).

Hydrogen was determined by combustion over hot copper oxide.

Hydrocarbons (remaining) were determined by combustion over hot platinum in the presence of excess oxygen, and computed as CH_4 and C_2H_6 from the measurement of contraction after burning and carbon dioxide produced by the combustion.

Nitrogen was computed by difference from 100.

Method II:

This method differs from I in the following respect:

Carbon monoxide and hydrogen were determined by burning together over hot copper oxide, with subsequent absorption of carbon dioxide produced.

Method III:

This method differs from I in the following respects:

Carbon monoxide, hydrogen, and hydrocarbons were burned in a single combustion over hot platinum in the presence of excess oxygen and computed as CO, H_2, and CH_4 from the observed contraction after combustion, carbon dioxide produced, and oxygen consumed.

Nitrogen was determined by measurement of the unreacted residue at the end of the analysis, corrected for known amounts of N_2 added during the analysis.

Of secondary importance, and applying to the tabulated data rather than the frequency plots, are arabic figures, which follow the roman numerals designating the major methods. The first figure indicates whether oxygen was absorbed by potassium pyrogallol (1) or in a chromous solution (2). The second figure indicates whether ethylene was absorbed in fuming sulfuric acid (1) or bromine (2).

Thus the abbrevation I–1–1 indicates that the carbon monoxide was determined by absorption, and that oxygen was absorbed in "pyro" and ethylene in fuming sulfuric acid. The abbreviation II–2–2 indicates that the carbon monoxide and hydrogen were determined with copper oxide, and that the oxygen was absorbed in a chromous solution and the ethylene in bromine.

VII. RESULTS OF THE COOPERATIVE ANALYSIS OF THE STANDARD GAS SAMPLE ASTM D-3-VII-1

1. MANNER OF PRESENTING THE ANALYTICAL DATA

All the analytical data submitted have been tabulated, and these tabulated data have been condensed by computing average values, which in turn have been tabulated. But contemplation of these tabulated data for some hours would not serve to reveal what may be seen at a glance when the same data are presented in a series of frequency-distribution plots. Accordingly, these plots, which amount to actual pictures of the analytical data, are presented first, with occasional reference to table 2, which gives the average values from each laboratory. Thereafter, table 3, which contains all of the analytical data reported, can be studied by those interested in any details that have not been shown by the plots. These two tables are given at the end of the paper.

Each circle appearing on the frequency-distribution plots represents a value derived from a single analysis (except for plots representing averages from each laboratory). The circles are plotted equidistant on the ordinate corresponding to their value. Thus the abscissas are values derived from the analyses, and the ordinates indicate the frequency with which these values occur. For example, in the top section of figure 1, nine circles on the ordinate corresponding to the value 0.650 indicate the fact that nine separate analyses yielded a value of 0.650 for the specific gravity of the sample. Similarly, 11 analyses yielded the value 0.651, 12 analyses yielded the value 0.652, and so on. This manner of plotting shows the distribution of all of the results at a glance, and forms the basis of a probability curve, of which the maxima are the most probable values. The effect of more than one major factor may also become apparent and at once suggest a further analysis or break down of the data. This has been done in the present instance by plotting the results obtained by the three major analytical methods both together and separately.

These graphical pictures not only save hours of study of the tabulated data, but actually make the significance of the data so self-evident that lengthy and detailed discussion of each figure is superfluous.

2. SPECIFIC GRAVITY CALCULATED FROM THE ANALYSES COMPARED WITH THE KNOWN SPECIFIC GRAVITY

The specific gravity (referred to dry CO_2—free air=1) was calculated from the following values given in International Critical Tables, volume 3, page 3, in terms of density.

CO_2	1.5290
O_2	1.1053
C_2H_4	0.97487
CO	.96713
H_2	.06952
CH_4	.5544
C_2H_6	1.0493
N_2	0.97208

These data are pictured in figure 1. The correct specific gravity is noted by the dotted line corresponding to the abscissa 0.6475. The measured value was obtained by comparing the weight of the gas with that of an equal volume of dry CO_2—free air. The measurements were made by E. C. Creitz at the National Bureau of Standards, who reported a value of $0.6475_0 \pm 0.00007$ (7 determinations).[3] It will be noted that values obtained by method I (absorption of CO) are generally too high, and are more widely scattered than those of methods II and III. Method III, which it will be remembered takes no account of ethane as such, appears to be the most reproducible; however, only three laboratories (four analysts) reported results obtained with this method, and it is possible that more data would have introduced a greater spread. The average value derived from 99 analyses in series I was 0.657 ± 0.007; the average from 96 analyses of series II was 0.648 to .004; the average from 28 analyses of series III was 0.648 ± 0.001. The plus or minus values indicate reproducibility expressed as the average deviation from the average.

[3] See footnote 2.

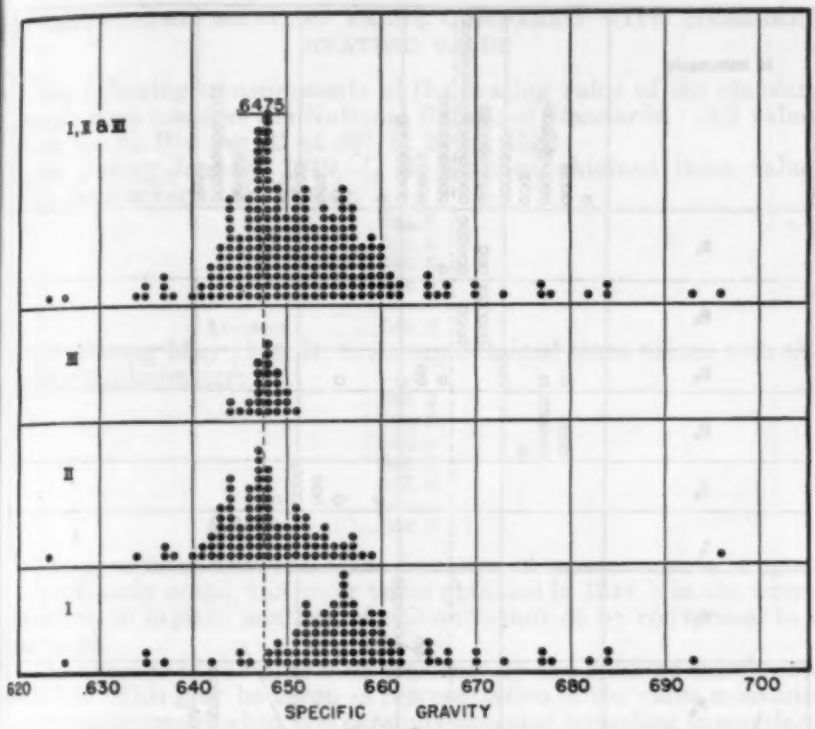


FIGURE 1.

Earlier in the history of Committee D–3, its subcommittee on the determination of specific gravity had discussed this measurement in terms of a tolerance of ±0.2 percent. Although this desideratum is met in the average deviation of the 28 analyses by method III, and roughly approached by method II, nevertheless, many separate determinations of these series lie far outside this tolerance. It is accordingly pertinent to compare these calculated results with those obtained by direct measurement of the specific gravity of this standard sample by means of the various instruments actually used for this purpose. This comparison is given in figure 2,[4] although the picture is not complete, as the determinations were all made in one laboratory by three men, and in consequence, the data are probably more compactly grouped than they would have been had 24 laboratories participated. Furthermore, only 10 determinations were made with each instrument. However, an idea of what might have been expected from various laboratories using various instruments may be seen by looking at the top section of figure 2. These data are taken from the original notebook of Smith, Eiseman, and Creitz during their measurements of the specific gravity of sample ASTM D–3–VII–1 by means of 11 different instruments operating on different basic principles. Again, no compliance with a ±0.2 percent desideratum is manifest. However, when these data are separated into groups showing the

[4] See footnote 2.

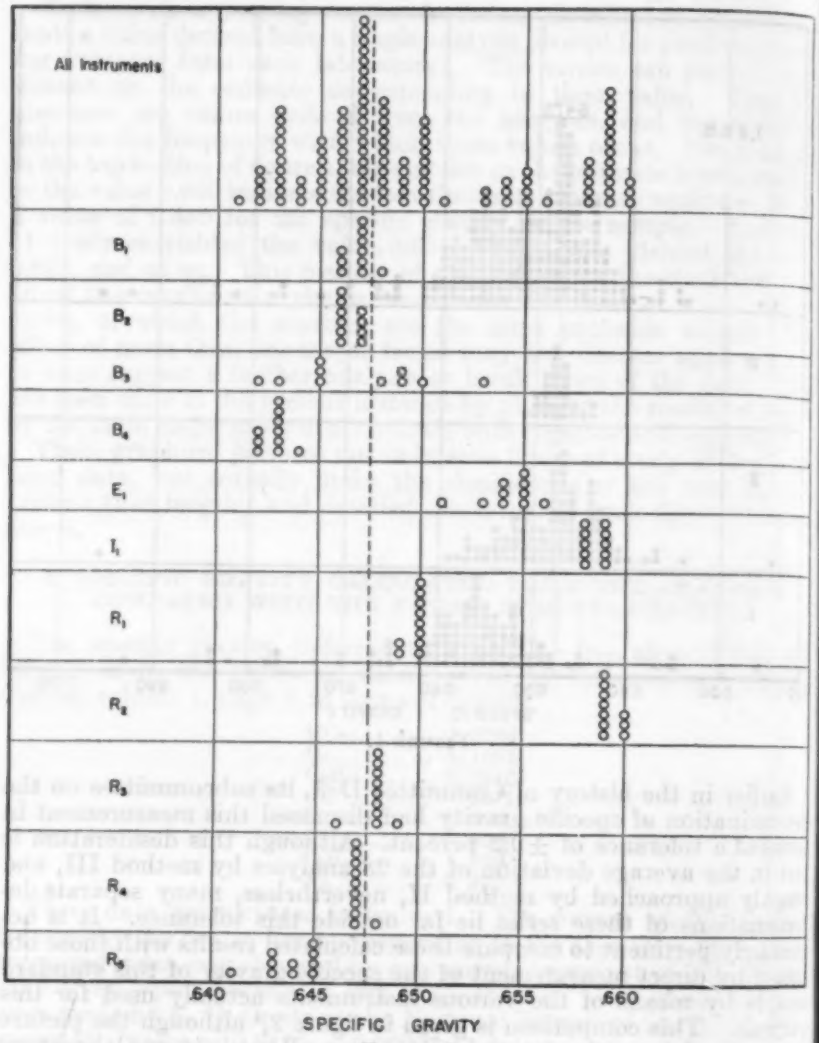


FIGURE 2.

behavior of each instrument, it appears that at least eight instruments give the desired reproducibility (in this instance, 0.001); and of these, four give the desired accuracy insofar as this particular gas sample is concerned. As the same sort of an analysis could be made by separating out the results of various laboratories in the case of the analytical data, we have not added greatly to our store of information other than by saying that certain combinations of the right apparatus, method, and operator can be found, but, in general, the over-all picture demands a more realistic treatment, which, for the present, means a more tolerant tolerance.

3. CALCULATED HEATING VALUE COMPARED WITH MEASURED HEATING VALUE

The following measurements of the heating value of the standard sample were made at the National Bureau of Standards. (All values given are in Btu per ft^3 at 60° F, 30 in. Hg.)

(a) During January 1940, J. H. Eiseman obtained these values with the Junker's calorimeter:

	549.8
	549.8
	549.5
	548.5
Average	549.4

(b) During May 1944, R. S. Jessup obtained these values with the Junker's calorimeter:

	549.2
	549.1
	548.9
	548.5
	547.5
Average	548.6

The agreement between these two sets of measurements is good; As previously noted, the lower value obtained in 1944 is in the wrong direction to explain any loss of carbon monoxide by conversion to a carbonyl.

The average of the nine measurements by the Junkers calorimeter is 549.0. This may be taken as representative of the value measured by this instrument when it is carefully operated according to standard procedures and with standard calibration of the meter. The agreement noted is probably better than would have appeared had 24 laboratories made this measurement.

The heating values calculated from all analyses (according to the directions given earlier) are given in figure 3, whereas those for each of the three principal analytical methods are given in figure 4. It will be noted that the greatest frequency of the calculated values appears to be a little to the left of the measured value. The values derived from method I show the greatest scattering and deviation from the measured value. The average value, 532.5, is 16.5 Btu too low. The scattering given by method II is not so bad; and the average value, 545, although 4 Btu low, is much nearer the measured value. The reproducibility yielded by method III is good; and the average value, 546.6, is still closer to the measured value (2.4 Btu low). In connection with method III, it is known in advance that the computed heating value will be in error, as the analysis is calculated as H_2, CO, and CH_4 only, whereas C_2H_6 was known to be present. The C_2H_6 present is calculated as $2CH_4$-H_2. The heating value of C_2H_6 is 1759, and that of $2CH_4$-H_2 is only 1675.4. The heating value calculated from such an analysis will accordingly be too low by 0.84 Btu for each 1 percent of C_2H_6. If the average value found for C_2H_6 by the 195 analyses of methods I and II is assumed to be nearly correct, the heating value calculated from method III would be too low by 2.2 Btu. The corrected value, 548.8, is in very comforting agreement with the measured value. Such a correction cannot be made unless

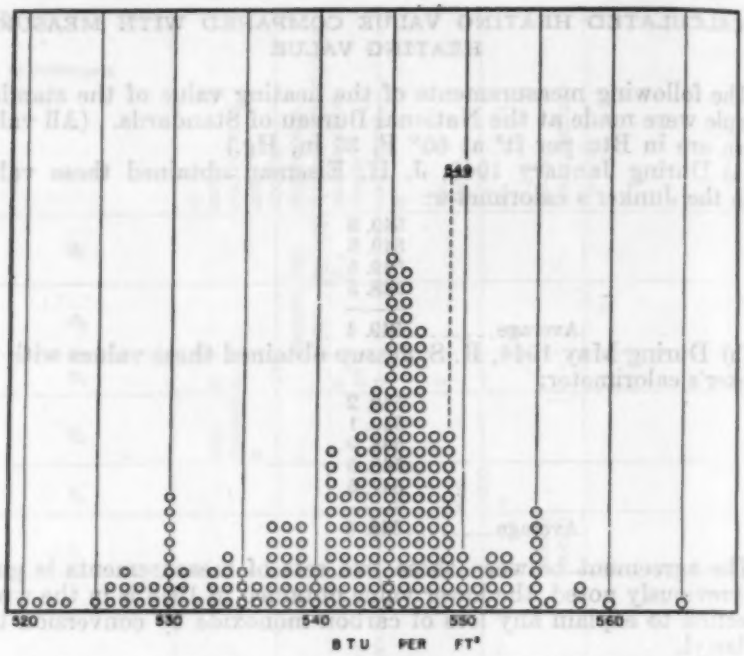


FIGURE 3.

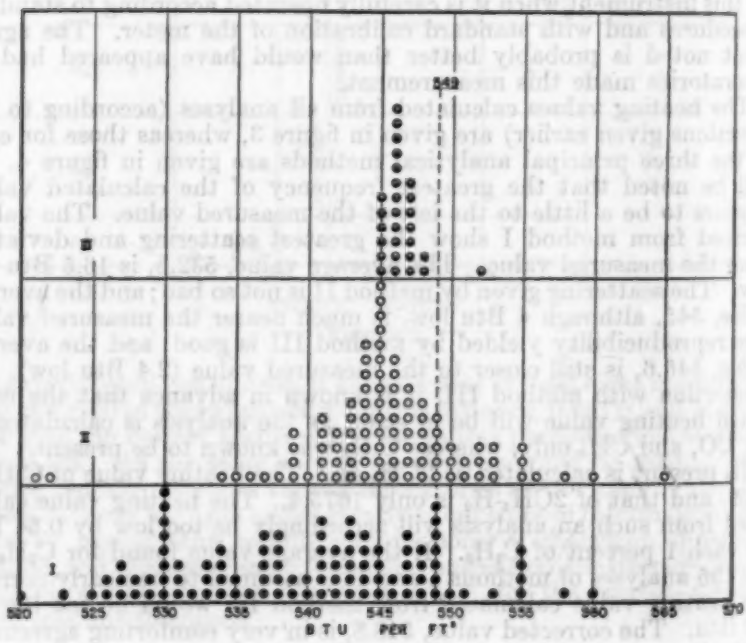


FIGURE 4.

the composition of the sample is known with respect to the heavier hydrocarbons, and if the illuminant fraction of a fuel gas is of complex composition, its heating value must be separately established before the calculated total heating value can be expected to check the measured value.

The latest draft of a proposed standard method for the determination of heating value, under consideration by Subcommittee 3 of ASTM D–3, assigns no tolerance to the measurement, but careful workers hope to obtain values within 0.5 percent of the actual heating value. This would be about 2.7 Btu in the case of the present sample. Method III is within this limit, method II is a little outside, and method I misses the desideratum somewhat.

It is entirely probable that a reproducibility of ± 0.5 percent may be attained between various laboratories in measuring the heating value of such a sample as this one by the Junker's calorimeter. However, it is interesting to speculate how close this may be to the true heating value. For example, in the present case, other information is available and is confusing:

1. If the meter used in determining the heating values reported is calibrated on open flow at the rate actually used during the calorimetric measurements, the heating value would be 551.2 instead of 549.0.

2. When the heating value was first measured by the Junker's calorimeter, it was also measured by a Thomas recording calorimeter, which in our laboratory is usually in close agreement with the Junker's instrument. The value obtained with the Thomas instrument was 554.

3. The heat of combustion of this sample was measured after it was passed through Ascarite to remove CO_2 and through anhydrous magnesium perchlorate to remove water vapor. The value obtained by J. W. Knowlton and F. D. Rossini, according to the usual procedures [5], was 692,270 ± 140 int. j/= mole (44.010 g) of CO_2 formed. If 1 Btu_{ASTM} is taken as equivalent to 1054.538 int. j, the heat of combustion measured is equivalent to 656.47 Btu per mole of CO_2 formed, which in turn is equivalent to 829.31 Btu/ft^3 of CO_2 found, referred to the ideal gas state at 0° C and 760 mm Hg (1 mole CO_2=22.4146 liters and 1 ft^3=28.3162 liters).

The late J. R. Branham of this Bureau made a careful volumetric measurement of the CO_2 produced by the complete combustion of this sample. Corrected for the CO_2 originally found and for the deviation of CO_2 from ideality (on the assumption that this deviation was proportional to the existing partial pressure of the CO_2), the stoichiometric relationship found was that 1 volume of gas yielded 0.7020 volume of CO_2. From this value and the heat of combustion, it would appear that the heating value of the sample was 542.67 Btu/ft^3, which is rather low in comparison with the other measurements.[6] On the basis of preliminary measurements of the additive volumes of CO_2 and the products of combustion, the corrected stoichiometric relation found was that 1 volume of gas yielded 0.7003 volume of CO_2, which

[5] Frederick D. Rossini, The heat of formation of water, BS J. Research 6, 1 (1931) RP259; The heats of combustion of methane and carbon monoxide, BS J. Research 6, 37 (1931) RP260; The heat of formation of water and the heats of combustion of methane and carbon monoxide. A correction. BS J. Research 7, 329 (1931) RP343.

[6] At the time the preliminary report of this work was released for study to Committee D–3, the heating value computed from the measured heat of combustion and volumetric measurement of CO_2 produced was erroneously reported as 553.8 Btu/ft.^{3}

in turn gives a computed heating value of 541.35 Btu/ft³, still lower than before.

Some time ago it was planned to measure gravimetrically the CO_2 produced from a cubic foot of the sample. This work has never been completed and remains on the after-the-war agenda. Perhaps the matter may be taken care of some day. Until then, it has been worthwhile to know how the results computed from the analyses check with those measured by the instrument most used for direct measurement of the heating value.

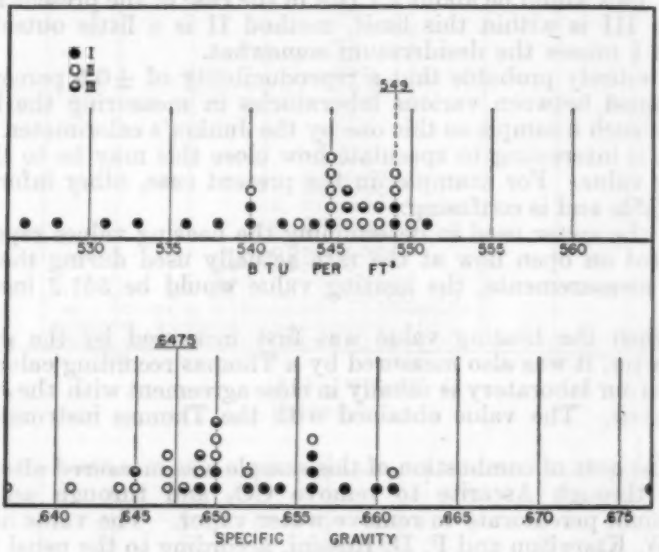


FIGURE 5.

4. COMPARISON OF LABORATORIES

Figure 5 gives an actual comparison of laboratories with respect to the calculation of both heating value and specific gravity. The points are each averages from the laboratories. The symbols of figure 4 are carried over to figure 5; closed circles represent values derived from analyses performed by method I; open circles are corresponding values derived from method II; and half-closed circles are values obtained from method III. The laboratory picture does not seem to alter the pattern already observed with respect to the three methods of analysis.

5. CARBON DIOXIDE

Data for CO_2 are given in figure 6. There are some rogues, but in general these data show very satisfactory reproducibility. Apparently this gas can be determined well enough. The country-wide result was 4.45 $\pm$0.05 percent. Translated to gravimetric terms, on the basis of the amount of sample used for analysis, $\pm$0.05 percent by volume may correspond to as little as 15 micrograms of CO_2. The volumetric determination which handles such small masses of CO_2

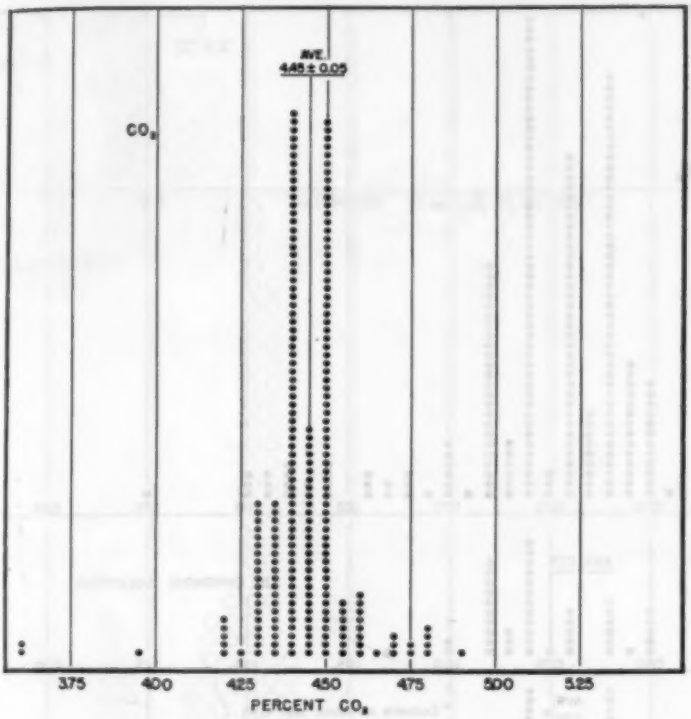


FIGURE 6.

is usually completed in a few minutes. This viewpoint is sometimes overlooked.

6. OXYGEN

The data for O_2 are given in figure 7. All values reported are grouped in the top section of this figure. The middle section gives values determined by chromous solutions, and the bottom section those obtained by alkaline pyrogallol solutions. There is no apparent significant difference between the two reagents as regards this particular gas. The chromous solution might be expected to remove more of the combustible consituents than the pyro solution (by physical solution), but the data available here do not indicate such a result and, therefore, attest the care with which this solution was equilibrated prior to analysis of this sample. The oxygen values in general are more widely scattered than would be expected from good analyses, and the high ones suggest air leakage during delivery to the analytical apparatus. However, there is no apparent correlation between high oxygen and high nitrogen, or between high oxygen and low heating value. As a matter of fact, the general frequency of values higher than expected indicates that something more than such leakage is involved.

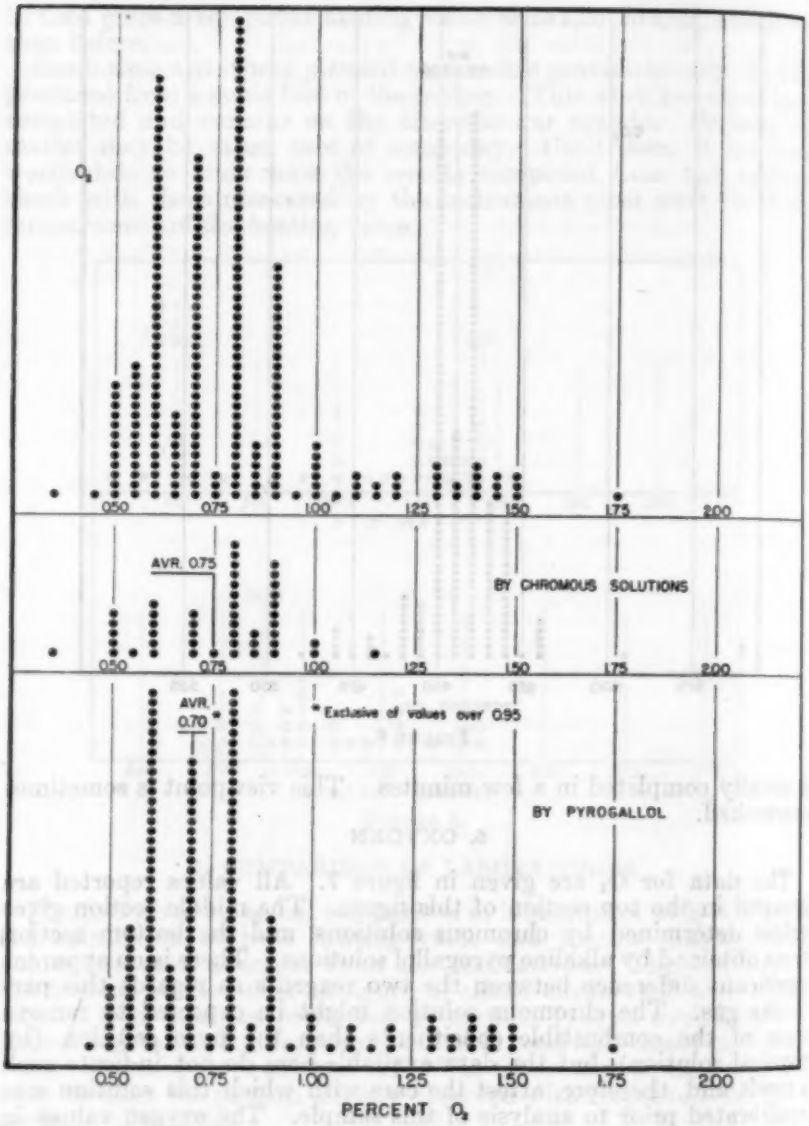


FIGURE 7.

7. ETHYLENE

Figure 8 gives the data for ethylene. The top section represents values obtained by reaction with bromine, and the bottom section gives all of the data reported. The effect of the lower values obtained by bromine is notable in the frequency plot of all the data. The values in general are not as widespread as might have been expected.

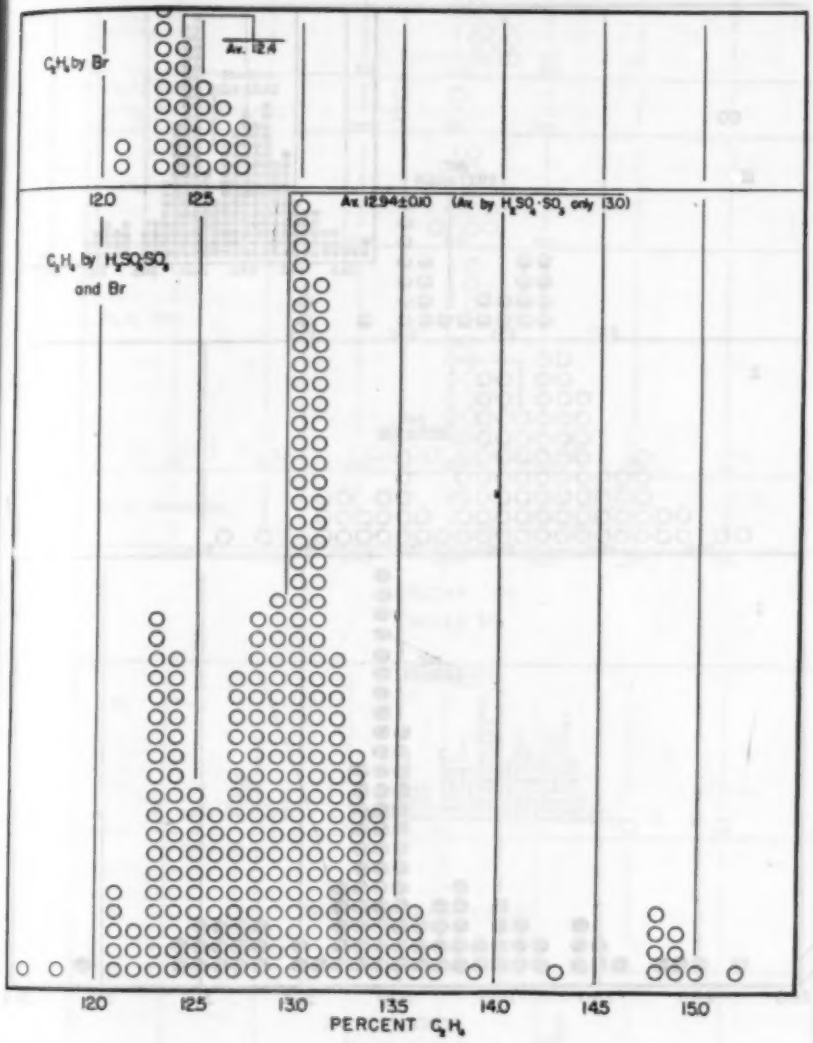


FIGURE 8.

8. CARBON MONOXIDE

Data for carbon monoxide are given in figures 9 and 10. The upper right-hand section of figure 9 includes the data from all three methods. The rest of the plot is divided into the three major methods employed. The absorption method shows the best reproducibility, even though it has resulted in the worst reproducibility in the matter of calculating specific gravity and heating value. The average value by absorption is notably higher than those obtained by the two methods of combustion.

Figure 10 is an analysis of the absorption data (method I of figure 9) with respect to the reagent used. The data are insufficient to permit

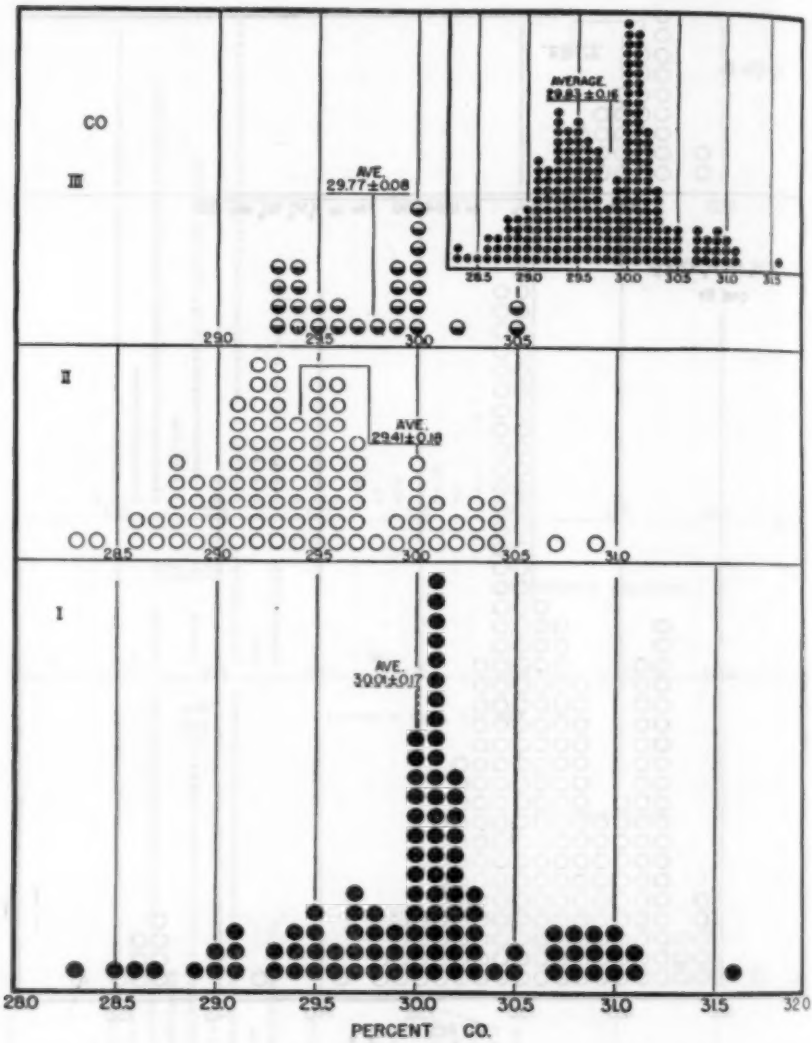


FIGURE 9.

drawing definite conclusions, although the higher values obtained with the ammoniacal reagent are evident.

9. HYDROGEN

The data for hydrogen are given in figure 11. Method III should not be compared with the other methods for the reasons previously noted. The lower hydrogen obtained with method I is to be compared with the higher CO obtained with this method. Reproducibility is better with method II than with method I.

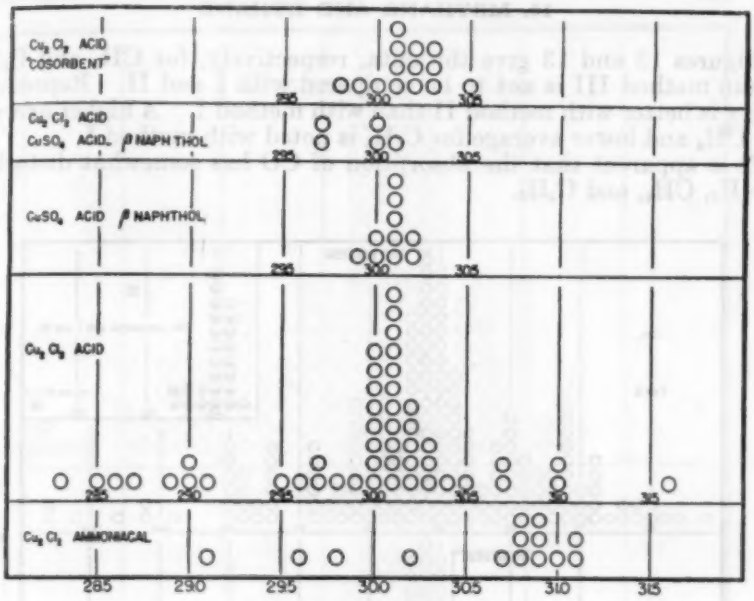


FIGURE 10.

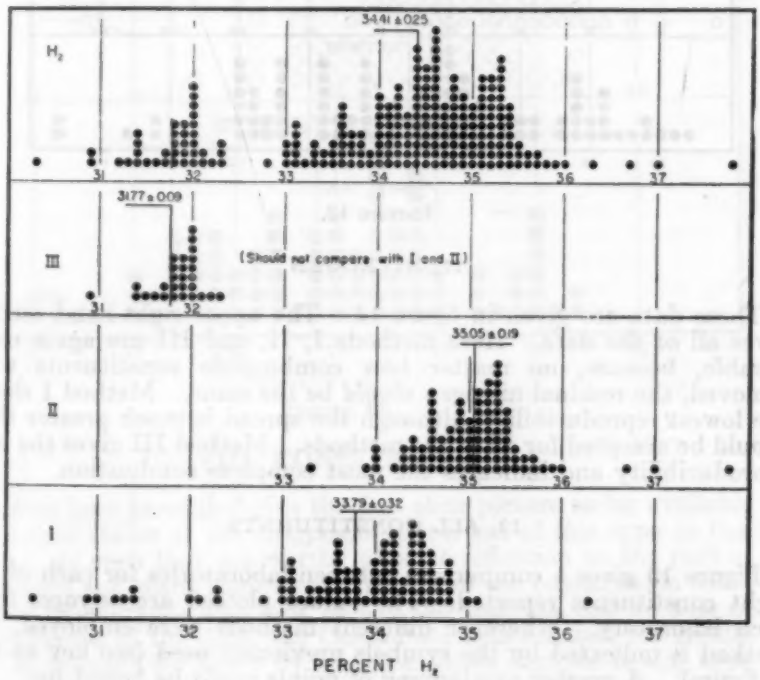


FIGURE 11.

10. METHANE AND ETHANE

Figures 12 and 13 give the data, respectively, for CH_4 and C_2H_6. Again method III is not to be compared with I and II. Reproducibility is better with method II than with method I. A higher average for CH_4 and lower average for C_2H_6 is noted with method I.

It is apparent that the absorption of CO has somewhat disturbed the H_2, CH_4, and C_2H_6.

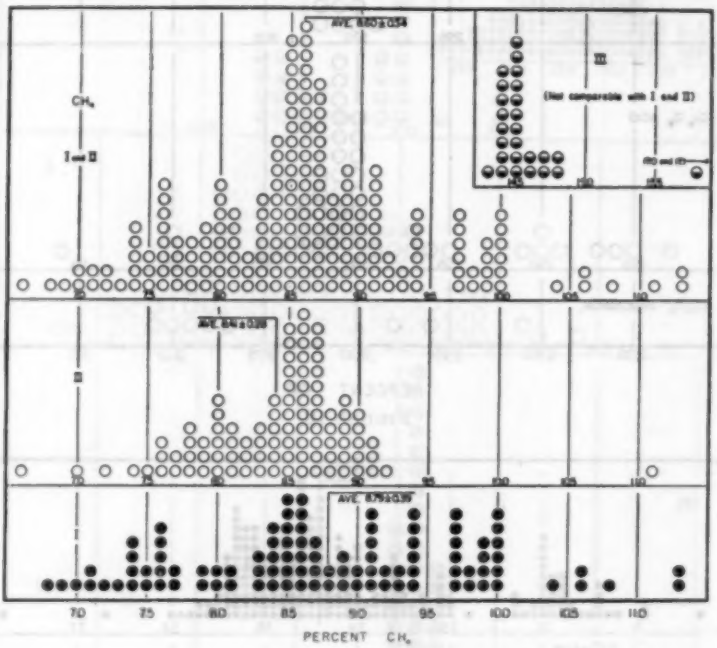


FIGURE 12.

11. NITROGEN

These data are given in figure 14. The upper right-hand section gives all of the data. Here methods I, II, and III are again comparable, because, no matter how combustible constituents were removed, the residual nitrogen *should* be the same. Method I shows the lowest reproducibility, although the spread is much greater than should be accepted for all of the methods. Method III gives the best reproducibility and indicates the most complete combustion.

12. ALL CONSTITUENTS

Figure 15 gives a comparison between laboratories for each of the eight constituents reported. The values plotted are *averages* from each laboratory. Wherever different methods were employed, the method is indicated by the symbols previously used (see key at top of figure). A greater overlapping of points could be hoped for.

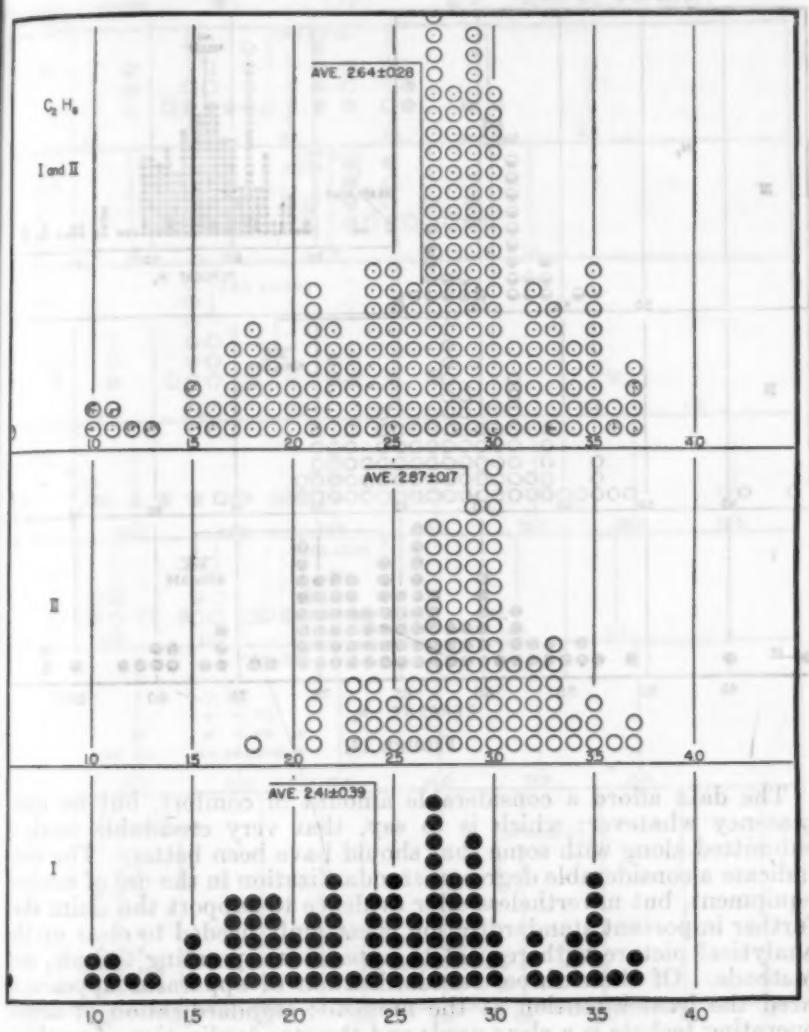


FIGURE 13.

VIII. CONCLUSIONS

The data here presented give the first clear picture so far available of the actual status of the analysis of a fuel gas of this type in this country. As such they are worthy of some reflection on the part of gas chemists and plant engineers. In view of the considerable effort expended by everyone who took part in the analyses, and because of the importance of the data, the Committee believes that the results should be released for study by all laboratories engaged in this type of volumetric gas analysis, even though the data constitute a preliminary report.

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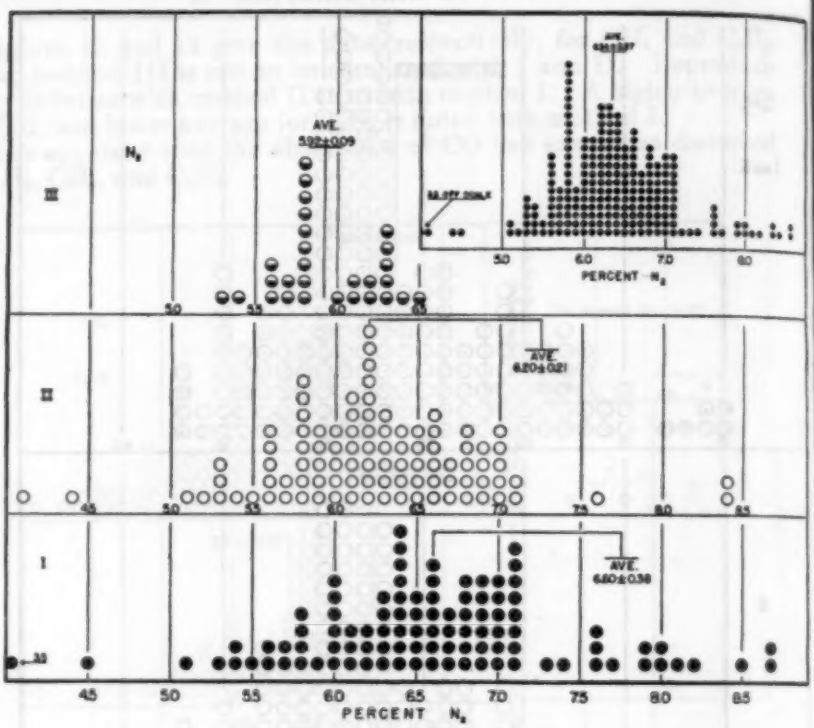

FIGURE 14.

The data afford a considerable amount of comfort, but no complacency whatever; which is to say, that very creditable work is submitted along with some that should have been better. The data indicate a considerable degree of standardization in the use of modern equipment, but nevertheless offer evidence to support the claim that further important standardization is certainly needed to clear up the analytical picture with respect to apparatus, operating technic, and methods. Of these three, standardization of apparatus appears to need the least attention at the moment; standardization of actual operating technic is a clear need; and the standardization of methods seems to be most needed.

IX. ADDENDA. A COMPARISON OF RESULTS OBTAINED BY THE MASS SPECTROMETER WITH ANALYSES BY THE CONVENTIONAL VOLUMETRIC METHODS OF ABSORPTION AND COMBUSTION

The mass spectrometer is the most important gas analysis apparatus to be made available during the past few years. It is capable of detecting and estimating an astonishingly large number of components in a mixture highly complex within a remarkably short time. Its scope is exceedingly wide, and it can make separations that would be well nigh impossible by other methods. It is sure to have extensive

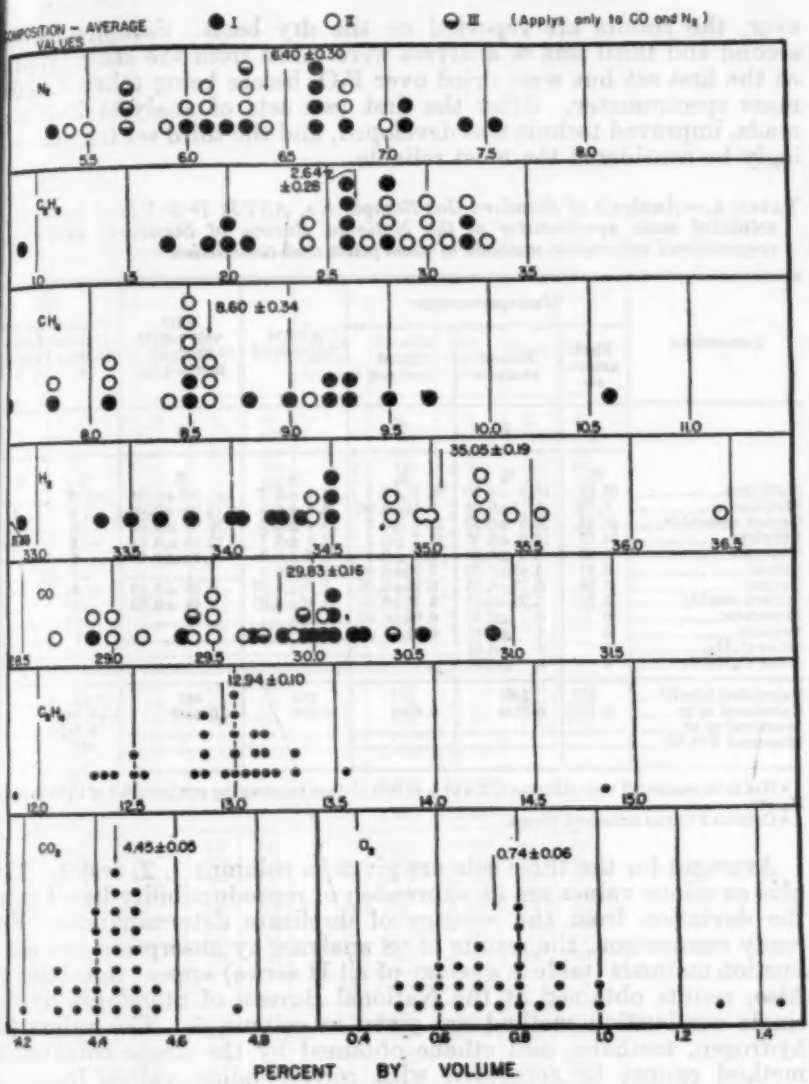

FIGURE 15.

use. For these reasons, it is of considerable interest to compare analyses made by it with those made by the conventional volumetric methods in the case of this nationally analyzed sample.

The analyses by the mass spectrometer are reported in table 4. They were made with the Consolidated Engineering Corporation mass spectrometer at the National Bureau of Standards. The instrument was in charge of A. Keith Brewer, operated by Vernon H. Dibeler, and computations were made by Dorothy I. Thompson. Three sets of analyses were made at different times. The first set was made with the original sample, containing some water vapor; how-

ever, the results are reported on the dry basis. Samples for th second and third sets of analyses were taken from the same cylinde as the first set but were dried over P_2O_5 before being taken into th mass spectrometer. After the first two sets of analyses had bee made, improved technic was developed, and the third set may accord ingly be considered the most reliable.

TABLE 4.—*Analysis of Standard Gas Sample No. ASTM D–3–VII–1 by the Co solidated mass spectrometer at the National Bureau of Standards and by th conventional volumetric methods of absorption and combustion*

Component	Mass spectrometer			ASTM Method II	NBS volumetric analysis method III	Column 3 minus column 4	Colum 3 minu colum 5
	First analysis	Second analysis	Third analysis				
	1	2	3	4	5	6	7
	%	%	%	%	%	%	%
Hydrogen	36.68	37.1 ±0.20	34.2 ±0.1	35.1 ±0.2	(31.95)±0.04	−0.9	
Methane	7.72	8.17±0.04	8.54±0.06	8.4 ±0.3	[a](14.39)±0.04	.1	
Carbon monoxide	25.42	26.5 ±0.10	29.7 ±0.2	29.4 ±0.2	29.96 ±0.03	.3	−0.3
Ethylene	14.17	13.0 ±0.10	12.7 ±0.2	12.9 ±0.1	12.96 ±0.02	−.2	−.3
Nitrogen	7.00	6.2 ±0.05	6.7 ±0.1	6.2 ±0.2	5.74 ±0.06	.5	.9
Ethane	3.31	3.43±0.02	3.20±0.08	2.9 ±0.2		.3	
Oxygen	0.38	0.27±0.05	0.20±0.02	0.74±0.07	0.55 ±0.03	−.54	−.3
Carbon dioxide	5.33	5.27±0.05	4.55±0.08	4.45±0.05	4.44 ±0.03	.10	.1
Propylene	0	0 ±0.01	0.04±0.02			.04	
Propane	0	0 ±0.01	0.21±0.01			.21	
Other C_nH_{2n}	0	0 ±0.01					
Other C_nH_{2n+2}	0	0 ±0.01					
Calculated Btu/ft³	557	550	552	545	546	[b]+3	
Calculated sp gr	0.6406	0.6339	0.6555	0.648	0.6476	[b]+0.009	
Measured sp gr						0.6475	
Measured Btu/ft³						549	

[a] Not to be compared with columns 1, 2, 3 or 4, as this method requires the computation of C_2H_6 as $2CH_4$–H_2, etc.

[b] Column 3 minus measured values.

Averages for the three sets are given in columns 1, 2, and 3. The plus or minus values are an expression of reproductibility based upon the deviation from the average of duplicate determinations. For ready comparison, the results of 98 analyses by absorption and combustion methods (table 2, average of all II series) appear in column 4. Also, results obtained at the National Bureau of Standards by the single combustion method are given in column 5. The values for hydrogen, methane, and ethane obtained by the single combustion method cannot be compared with corresponding values from the other methods, as all of the combustible gases (except ethylene and homologues) are computed as H_2, CO, and CH_4. Thus C_2H_6 is computed as $2CH_4$–H_2, C_3H_8 as $3CH_4$–$2H_2$, and so on. However, the values so obtained can be used in computing heating value and specific gravity and in studying combustion characteristics.

The three sets of analyses by the mass spectrometer, which were made at various times during 1944, differ among themselves by as much as 3 or 4 percent in some instances. The first analysis yielded a calculated heating value 8 Btu higher than the measured value and a calculated specific gravity 0.007 below the measured value. The second analysis gave a calculated heating value only 1 Btu higher than the measured value, but a specific gravity 0.013 lower than the

TABLE 2.—*Analysis of Standard Gas Samp*

Condensed table giving average values of 288 analyses by different apparatus and methods.

The specific gravity of this gas was measured by E. C. Crelts at the National Bureau of Standards. The measured value was 0.64750±0.00007.

The heating value was measured independently by J. H. Eiseman and Ralph S. Jessup with the Junker's calorimeter at the National Bureau of Standards. The measured value was 549.0±0.6 Btu/ft³.

Condensed key to methods of analysis:

I. CO by absorption, H_2 by CuO, $CH_4+C_2H_6$ by slow combustion.

II. $CO+H_2$ by CuO, $CH_4+C_2H_6$ as in II.

III. $CO+H_2+CH_4+$heavier C_nH_{2n+2} by slow combustion, calculated as $CO+H_2+CH_4$ only.

First set of arabic numerals: 1-, O_2 by pyro; 2-, O_2 by chromous solution.

Second set of arabic numerals: 1-, C_2H_4 by $H_2SO_4.SO_3$; 2-, C_2H_4 by bromine.

Line	Laboratory	Method	Apparatus	Carbon dioxide					Oxygen					Ethylene					Carbon monoxide						
				Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Ar
					%	%	%	%		%	%	%	%		%	%	%	%		%	%	%	%		
1	1	I-1-1	V_1R_1Hg	7	4.46	±0.03	4.50	4.35	7	0.68	±0.04	0.75	0.60	7	12.84	±0.06	12.90	12.70	7	30.19	±0.10	30.30	30.10	7	
2	2	I-1-1	$V_1R_1H_2O$ acid	3	4.35	±.03	4.40	4.30	3	.92	±.08	1.05	.80	3	13.08	±.04	13.10	13.00	3	29.93	±.19	30.15	29.65	3	
3	7	I-1-1	V_2R_2Hg	4	4.19	±.12	4.3	3.96	4	.98	±.09	1.15	.84	4	12.83	±.10	12.98	12.7	4	29.70	±.41	30.17	29.13	4	
4	8	I-1-1	V_1R_1Hg	10	4.43	±.06	4.5	4.3	10	.66	±.06	0.80	.60	10	13.21	±.09	13.4	13.0	10	30.08	±.07	30.2	29.9	10	
5	12	I-1-1	V_1R_1Hg	10	4.44	±.04	4.52	4.33	10	.80	±.02	.82	.72	10	13.10	±.07	13.27	12.97	10	30.53	±.45	31.55	29.71	10	
6	15	I-1-1	V_1R_1Hg	6	4.48	±.06	4.6	4.4	6	.71	±.08	.9	.6	6	12.98	±.09	13.1	12.8	6	30.10	±.10	30.3	29.9	6	
7	23	I-1-1	$V?R_1Hg$	10	4.77	±.04	4.91	4.70	10	• 1.46	±.08	1.77	1.36	10	14.84	±.18	15.21	14.26	10	28.92	±.32	29.61	28.25	10	
	Average of I-1-1 series			50	4.49	±0.05			40	0.76	±0.05			50	13.40	±0.09			50	29.92	±0.24			50	
8	4	I-2-1	V_1R_1Hg	7	4.5	±0.04	4.6	4.3	7	0.9	±0.09	1.0	0.7	7	13.0	±0.04	13.1	13.0	7	30.1	±0.19	30.5	29.8	7	
9	6	I-2-1	V_1R_1Hg	5	4.54	±.03	4.6	4.5	5	.88	±.06	1.0	.8	5	13.29	±.11	13.45	13.10	5	29.87	±.14	30.05	29.65	5	
10	17	I-2-1	V_1R_1Hg	10	4.54	±.06	4.65	4.43	10	.80	±.03	0.9	.7	10	13.56	±.10	13.85	13.35	10	29.36	±.11	29.55	29.10	10	
	Average of I-2-1 series			22	4.53	±0.05			22	0.85	±0.06			22	13.32	±0.08			22	29.71	±0.15			22	
11	2	I-1-2	$V_1R_1H_2O$ acid	7	4.32	±0.06	4.40	4.20	7	0.99	±0.10	1.10	0.80	7	12.52	±0.13	12.65	12.55	7	30.04	±0.10	30.25	29.80	7	
12	19	I-1-2	$V?R_1H_2O$ salt	10	4.46	±.03	4.50	4.40	10	.80	±.07	0.90	.70	10	12.33	±.08	12.50	12.11	10	30.91	±.11	31.10	30.72	10	
13	22	I-1-2	V_1R_1Hg	10	4.38	±.05	4.5	4.2	10	• 1.29	±.09	1.5	1.0	10	12.38	±.08	12.5	12.3	10	30.11	±.09	30.3	30.0	10	
	Average of I-1-2 series			27	4.39	±0.05			17	0.88	±0.08			27	12.40	±0.10			27	30.39	±0.10			27	
14	20	I-2-2	Bone-Wheeler	2	4.31	±0.05			2	0.75	±0.07			2	12.52	±0.05			2	30.24	±0.07			2	
	Average of all I series			101	4.47	±0.05			81	0.81	±0.06			101	12.97	±0.09			101	30.01	±0.17			101	
15	1	II-1-1	V_1R_1Hg	9	4.42	±0.03	4.50	4.40	9	0.75	±0.08	0.85	0.60	9	12.83	±0.05	13.00	12.70	9	29.16	±0.07	29.30	29.00	9	
16	3	II-1-1	V_2 or $_2R_1Hg$	10	4.5	±.02	4.5	4.4	10	.8	±.03	.9	.6	10	13.0	±.11	13.4	12.8	10	29.9	±.20	29.6	30.2	10	
17	9	II-1-1	V_1R_1Hg	8	4.42	±.07	4.5	4.3	8	.68	±.08	.8	.6	8	13.28	±.11	13.5	13.2	8	29.41	±.06	29.5	29.3	8	
18	10	II-1-1	V_1R_1Hg	9	4.45	±.08	4.52	4.31	10	.62	±.06	.69	.51	10	13.05	±.18	13.53	12.76	10	29.63	±.39	30.74	28.65	10	
19	13	II-1-1	V_1R_1Hg	10	4.34	±.06	4.4	4.2	10	.78	±.07	.9	.6	10	13.14	±.11	13.3	12.7	10	29.02	±.16	29.3	28.7	10	
20	14	II-1-1	V_1R_1Hg	10	4.49	±.04	4.55	4.40	10	.67	±.05	.80	.60	10	12.83	±.04	12.91	12.76	10	29.52	±.12	29.90	29.25	10	
21	16	II-1-1	V_1R_1Hg	10	4.50	±.01	4.55	4.40	10	.65	±.05	.70	.60	10	12.30	±.19	12.70	12.05	10	30.05	±.30	30.50	29.50	10	
22	21	II-1-1	V_1R_1Hg	9	4.41	±.02	4.5	4.4	9	.84	±.15	1.20	.60	9	13.13	±.21	13.6	13.0	9	28.97	±.26	29.3	28.4	9	
	Average of II-1-1 series			75	4.45	±0.05			76	0.73	±0.07			76	12.94	±0.14			76	29.47	±0.20			76	
23	4	II-2-1	V_1R_1Hg	8	4.5	±0.05	4.5	4.3	8	0.8	±0.06	0.9	0.7	8	13.0	±0.06	13.1	12.9	8	29.5	±0.12	29.6	29.1	8	
24	18	II-2-1	V_1R_1Hg	5	4.48	±.06	4.61	4.38	5	.72	±.15	1.15	.53	5	13.00	±.15	13.21	12.67	5	28.72	±.24	29.15	28.3	5	
25	18	II-2-1	V_1R_1Hg	5	4.39	±.05	4.46	4.33	5	.48	±.08	0.52	.32	5	12.57	±.21	12.81	12.34	5	29.51	±.10	29.67	29.34	5	
26	18	II-2-1	V_1R_1Hg	5	4.45	±.05	4.5	4.4	5	.58	±.04	.70	.50	5	13.13	±.09	13.3	13.0	5	28.98	±.18	30.9	28.8	5	
	Average of II-2-1 series			23	4.46	±0.05			23	0.66	±0.08			23	12.93	±0.12			23	29.22	±0.16			23	
	Average of all II series			98	4.45	±0.05			98	0.74	±0.07			99	12.94	±0.12			99	29.41	±0.18			99	
	Average of I and II series																		200	29.71	±.17			200	
27	5	III-1-1	V_1R_1Hg	10	4.39	±0.02	4.43	4.35	10	0.61	±0.04	0.69	0.59	10	13.08	±0.05	13.18	13.00	10	29.39	±0.08	29.59	29.25	10	
28	11	III-1-1	V_1R_1Hg	3	4.30	±.07	4.37	4.20	3	.53	±.05	.59	.45	3	11.86	±.20	12.15	11.59	3	30.41	±.13	30.53	30.21	3	
29	24	III-1-1	V_1R_1Hg	10	4.44	±.03	4.39	4.49	10	.55	±.03	.49	.61	10	12.96	±.02	13.00	12.90	10	29.96	±.03	30.02	29.91	10	
30	24	III-1-1	V_1R_1Hg	5	4.44	±.05	4.51	4.35	5	.51	±.03	.57	.54	5	12.78	±.04	12.86	12.71	5	29.74	±.15	30.03	29.50	5	
	Average of III-1-1 series			28	4.41	±0.03			28	0.56	±0.05			28	12.86	±0.05			28	29.77	±0.08			28	
	Average of I, II, and III series			227	4.453	±.05	4.77	4.19	208	.738	±.06			228	12.94	±.10			228	29.83	±.16			228	
	Maxima-minima						4.91	3.96				1.77	0.32				15.21	11.59				31.55	28.25	(Excl. III)	
	Next to maxima-minima						4.65	4.20				1.50	.45				13.85	12.11				31.10	28.30	(Excl. III)	

• Omitted from average.

TABLE 2.—*Analysis of Standard Gas Sample ASTM D-3-VII-1, (carburette*

Condensed table giving average values of 288 analyses by different apparatus and methods.
The specific gravity of this gas was measured by E. C. Creitz at the National Bureau of Standards. The measured value was 0.64750±0.00007.
The heating value was measured independently by J. H. Eiseman and Ralph S. Jessup with the Junker's calorimeter at the National Bureau of Standards. The measured value was 549.0±0.6 Btu/ft³.
Condensed key to methods of analysis:
I. CO by absorption, H_2 by CuO, $CH_4+C_2H_4$ by slow combustion.
II. $CO+H_2$ by CuO, $CH_4+C_2H_4$ as in II.
III. $CO+H_2+CH_4$+heavier C_nH_{2n+2} by slow combustion, calculated as $CO+H_2+CH_4$ only.
First set of arabic numerals: 1-, O_2 by pyro; 2-, O_2 by chromous solution.
Second set of arabic numerals: 1-, C_2H_4 by $H_2SO_4.SO_3$; 2-, C_2H_4 by bromine.

Key to apparatus:
V_1—Equipped with pressure-
V_2—Volumes corrected for ter
V_3—Volumes not corrected fo
V_4—Constant volume apparat
R_1—Pipettes connected to bu
R_2—Single pipette connected
R_3—Pipettes separate from bu
The last symbol designates th

Ethylene					Carbon monoxide					Hydrogen						
ber de-ni-ons	Amount	Aver-age devia-tion	Max	Min	Number of de-termi-nations	Amount	Aver-age devia-tion	Max	Min	Number of de-termi-nations	Amount	Aver-age devia-tion	Max	Min	Number of de-termi-nations	Ar
	%	%	%	%		%	%	%	%		%	%	%	%		
7	12.84	±0.06	12.90	12.70	7	30.19	±0.10	30.30	30.10	7	33.63	±0.10	33.75	33.50	7	
3	13.06	±.04	13.10	13.00	3	29.93	±.19	30.15	29.65	3	33.98	±.26	34.20	33.60	3	
4	12.83	±.10	12.98	12.7	4	29.70	±.41	30.17	29.13	4	34.50	±.29	34.03	32.99	4	
10	13.21	±.09	13.4	13.0	10	30.08	±.07	30.2	29.9	10	34.5	±.20	34.8	34.2	10	
10	13.10	±.07	13.27	12.97	10	30.53	±.45	31.55	29.71	10	34.03	±.75	36.25	33.07	10	
6	12.98	±.09	13.1	12.8	6	30.10	±.10	30.3	29.9	6	34.35	±.30	34.8	33.7	4	
10	14.84	±.18	15.21	14.26	10	28.92	±.32	29.61	28.25	10	31.58	±.73	34.29	30.91	10	
50	13.40	±0.09	-------	-------	50	29.92	±0.24	-------	-------	50	33.57	±0.42	-------	-------	48	
7	13.0	±0.04	13.1	13.0	7	30.1	±0.19	30.5	29.8	7	34.3	±0.27	35.0	34.1	7	
5	13.29	±.11	13.45	13.10	5	29.87	±.14	30.05	29.65	5	33.79	±.21	34.00	33.45	5	
10	13.56	±.10	13.85	13.35	10	29.36	±.11	29.55	29.10	10	32.91	±.26	33.30	32.28	10	
22	13.32	±0.08	-------	-------	22	29.71	±0.15	-------	-------	22	33.55	±0.25	-------	-------	22	
7	12.52	±0.13	12.65	12.55	7	30.04	±0.10	30.25	29.80	7	34.19	±0.23	34.70	33.75	7	
10	12.33	±.08	12.50	12.11	10	30.91	±.11	31.10	30.72	10	34.50	±.13	34.80	34.23	10	
10	12.38	±.08	12.5	12.3	10	30.11	±.09	30.3	30.0	10	34.48	±.21	34.8	34.1	10	
27	12.40	±0.10	-------	-------	27	30.39	±0.10	-------	-------	27	34.41	±0.19	-------	-------	27	
2	12.52	±0.05	-------	-------	2	30.24	±0.07	-------	-------	2	33.34	±0.01	-------	-------	2	
101	12.97	±0.09	-------	-------	101	30.01	±0.17	-------	-------	101	33.75	±0.32	-------	-------	99	
9	12.83	±0.05	13.00	12.70	9	29.16	±0.07	29.30	29.00	9	35.27	±0.06	35.35	35.10	9	
10	13.0	±.11	13.4	12.8	10	29.9	±.20	29.6	30.2	10	34.4	±.15	34.6	34.0	10	
8	13.28	±.11	13.5	13.2	8	29.41	±.06	29.5	29.3	8	34.8	±.10	34.9	34.6	8	
10	13.05	±.18	13.53	12.76	10	29.63	±.39	30.74	28.65	10	34.82	±.35	34.75	33.93	10	
10	13.14	±.11	13.3	12.7	10	29.02	±.16	29.3	28.7	10	34.96	±.13	35.2	34.7	10	
10	12.83	±.04	12.91	12.76	10	29.52	±.12	29.90	29.25	10	35.25	±.08	35.44	35.09	10	
10	12.30	±.19	12.70	12.05	10	30.05	±.30	30.50	29.50	10	35.40	±.27	35.90	34.90	7	
9	13.13	±.21	13.6	13.0	9	28.97	±.26	29.3	28.4	9	34.42	±.18	34.7	34.0	9	
76	12.94	±0.14	-------	-------	76	29.47	±0.20	-------	-------	76	34.92	±0.17	-------	-------	73	
8	13.0	±0.06	13.1	12.9	8	29.5	±0.12	29.6	29.1	8	35.0	±0.08	35.1	34.9	8	
5	13.00	±.15	13.21	12.67	5	28.72	±.24	29.15	28.3	5	36.43	±.62	37.78	35.29	5	
5	12.57	±.21	12.81	12.34	5	29.51	±.10	29.67	29.34	5	35.56	±.21	36.03	35.26	5	
5	13.13	±.09	13.3	13.0	5	28.98	±.18	30.9	28.8	5	35.25	±.18	35.6	33.3	5	
23	12.93	±0.12	-------	-------	23	29.22	±0.16	-------	-------	23	35.49	±0.25	-------	-------	23	
99	12.94	±0.12	-------	-------	99	29.41	±0.18	-------	-------	99	35.05	±0.19	-------	-------	96	
----	----------	-------	-------	-------	200	29.71	±.17	-------	-------	200	34.41	±.25	-------	-------	195	
10	13.08	±0.05	13.18	13.00	10	29.39	±0.08	29.59	29.25	10	31.77	±0.08	31.99	31.37	10	
3	11.86	±.20	12.15	11.59	3	30.41	±.13	30.53	30.21	3	30.62	±.19	30.42	30.91	3	
10	12.96	±.02	13.00	12.90	10	29.96	±.03	30.02	29.91	10	31.95	±.04	32.03	31.91	10	
5	12.78	±.04	12.86	12.71	5	29.74	±.15	30.03	29.50	5	32.09	±.14	32.29	31.89	5	
28	12.86	±0.05	-------	-------	28	29.77	±0.08	-------	-------	28	31.77	±0.00	-------	-------	28	
228	12.94	±.10	-------	-------	228	29.83	±.16	-------	-------	228	----------	-------	-------	-------	223	
----	----------	-------	15.21	11.59	----------	----------	-------	31.55	28.25	(Excl. III)	----------	-------	37.78	30.91	(Excl. III)	
----	----------	-------	13.85	12.11	----------	----------	-------	31.10	28.30	(Excl. III)	----------	-------	36.25	32.28	(Excl. III)	

, *(carburetted water-gas type)*

ns:
d with pressure-temperature compensator.
corrected for temperature-pressure changes.
not corrected for temperature-pressure changes.
volume apparatus.
connected to burette by manifold.
ette connected to burette.
eparate from burette.
ol designates the confining fluid.

Methane					Ethane					Nitrogen					Btu/ft³—60°		
Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Btu/ft³	A d
	%	%	%	%		%	%	%	%		%	%	%	%		%	
7	8.77	±0.14	9.10	8.60	7	2.59	±0.12	2.80	2.35	7	6.85	±0.19	7.10	6.45	7	540	
3	9.22	±.44	9.70	8.55	3	1.90	±.33	2.40	1.75	3	6.63	±.24	7.00	6.40	3	536	
4	10.59	±.37	11.32	10	4	.89	±.18	1.06	3.4	4	7.33	±.56	8.19	6.32	4	526	
10	7.8	±.6	9.0	6.9	10	3.2	±.3	3.5	2.6	10	6.2	±.35	7.1	5.6	10	549	
10	9.33	±.88	10.75	7.48	10	2.14	±.63	3.71	1.08	10	6.30	±.97	7.35	4.53	10	533	
4	9.5	±1.4	11.3	6.8	4	2.6	±.5	3.7	1.9	4	5.3	±.9	6.6	3.5	4	551	
10	9.18	±.45	9.97	8.33	10	1.09	±.22	2.15	1.48	10	7.55	±.79	8.72	5.36	10	549	
48	9.01	±0.60	------	------	48	2.25	±0.58	------	------	48	6.64	±0.56	------	------	48	541.8	
7	8.5	±0.07	8.7	8.4	7	2.6	±0.10	2.8	2.5	7	6.0	±0.29	6.5	5.3	7	541.5	
5	8.48	±.10	8.7	8.3	5	2.59	±.10	2.65	2.35	5	6.56	±.19	6.85	6.35	5	544	
10	9.72	±.23	10.01	9.35	10	2.02	±.16	2.34	1.73	10	7.11	±.27	7.67	6.70	10	545	
22	9.05	±0.15	------	------	22	2.33	±0.15	------	------	22	6.63	±0.26	------	------	22	544	
7	9.32	±0.34	9.75	8.80	7	1.98	±0.23	2.35	1.70	7	6.64	±0.16	6.95	6.25	7	531	
10	7.47	±.19	8.03	7.10	10	2.84	±.20	3.20	2.40	10	6.69	±.13	7.07	6.40	10	528	
10	8.11	±.29	8.6	7.6	10	3.15	±.27	3.6	2.8	10	6.10	±.14	6.4	5.8	10	538	
27	8.19	±0.27	------	------	27	2.73	±0.27	------	------	27	6.46	±0.14	------	------	27	532.5	
2	8.97	±0.05	------	------	2	2.80	------	------	------	2	7.07	±0.005	------	------	2	539.6	
99	8.79	±0.39	------	------	99	2.41	±0.39	------	------	99	6.60	±0.38	------	------	99	538.7	
9	8.59	±0.10	8.75	8.40	9	2.87	±0.08	3.00	2.80	9	6.12	±0.08	6.30	6.00	9	545	
10	8.1	±.41	8.9	7.2	10	3.1	±.15	3.5	2.8	10	6.3	±.23	6.8	5.8	10	546	
8	8.6	±.30	9.0	8.1	8	2.4	±.20	2.7	2.1	8	6.4	±.30	6.8	5.2	8	545	
10	8.07	±.38	9.03	7.71	10	3.20	±.21	3.68	2.74	10	6.29	±.34	7.12	5.57	10	549	
10	8.54	±.30	8.9	7.8	10	2.43	±.22	2.7	1.8	10	6.78	±.43	8.4	6.3	10	540	
10	8.51	±.07	8.60	8.39	10	2.97	±.07	3.11	2.83	10	5.82	±.05	5.90	5.64	10	547	
7	7.75	±.27	8.65	7.00	7	3.25	±.33	3.70	2.65	7	6.00	±.29	6.35	5.35	7	538	
9	8.41	±.12	8.6	8.2	9	2.79	±.11	3.0	2.4	9	7.02	±.20	7.9	6.8	9	543	
73	8.33	±0.24	------	------	73	2.88	±0.17	------	------	73	6.35	±0.24	------	------	73	544.4	
8	8.6	±0.14	9.0	8.3	8	2.7	±0.14	3.0	2.5	8	5.9	±0.12	6.2	5.6	8	545	
5	8.54	±1.26	11.07	6.64	5	2.78	±.37	3.30	2.28	5	5.33	±.90	7.58	4.09	5	548	±
5	9.08	±.08	9.23	8.98	5	2.95	±.05	2.99	2.82	5	5.46	±.27	5.98	5.13	5	549	
5	8.50	±.30	8.9	7.9	5	3.03	±.13	3.2	2.9	5	6.10	±.30	6.5	5.5	5	550	
23	8.67	±0.40	------	------	23	2.84	±0.17	------	------	23	5.72	±0.13	------	------	23	547.6	
96	8.41	±0.28	------	------	96	2.87	±0.17	------	------	96	6.20	±0.21	------	------	96	545.0	
195	8.60	±.34	------	------	195	2.64	±.28	------	------	195	6.40	±0.30	------	------	195	543.1	
10	14.50	±0.04	14.59	14.39	------	------	------	------	------	10	6.25	±0.05	6.36	6.10	10	547	
3	16.62	±.51	17.06	15.84	------	------	------	------	------	3	5.70	±.27	6.10	5.33	3	548	
10	14.39	±.04	14.50	14.34	------	------	------	------	------	10	5.74	±.06	5.82	5.61	10	546	
5	14.70	±.07	14.80	14.51	------	------	------	------	------	5	5.74	±.12	5.97	5.44	5	546	
28	14.72	±0.10	------	------	------	------	------	------	------	28	5.92	±0.09	------	------	28	546.6	
223	------	±.31	------	------	195	2.64	------	------	------	223	6.34	±.27	------	------	223	543.5	
(Excl. III)	------	------	11.32	6.64	------	------	------	3.71	1.08	------	------	------	8.72	3.5	------	------	
(Excl. III)	------	------	11.07	6.8	------	------	------	3.68	1.70	------	------	------	8.4	4.09	------	------	

retted water-gas type)

ure-temperature compensator.
r temperature-pressure changes.
d for temperature-pressure changes.
paratus.
burette by manifold.
ted to burette.
n burette.
s the confining fluid.

Methane				Ethane					Nitrogen					Btu/ft³—60°, 30 in. Hg. Sat.					Specific gravity				
Amount	Average deviation	Max	Min	Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Amount	Average deviation	Max	Min	Number of determinations	Btu/ft³	Average deviation	Max	Min	Number of determinations	Specific gravity	Average deviation	Max	Min
%	%	%	%		%	%	%	%		%	%	%	%			%	%	%			%	%	%
8.77	±0.14	9.10	8.60	7	2.59	±0.12	2.80	2.35	7	6.85	±0.19	7.10	6.45	7	540	±3	543	537	7	0.656	±0.002	0.659	0.652
9.22	±.44	9.70	8.55	3	1.90	±.33	2.40	1.75	3	6.63	±.24	7.00	6.40	3	536	±2	538	533	3	.652	±.002	.654	.650
10.59	±.37	11.32	10	4	.89	±.18	1.06	3.4	4	7.33	±.56	8.19	6.32	4	526	±3	530	520	4	.650	±.004	.655	.642
7.8	±.6	9.0	6.9	10	3.2	±.3	3.5	2.6	10	6.2	±.35	7.1	5.6	10	549	±2	555	548	10	.656	±.006	.670	.651
9.33	±.88	10.75	7.48	10	2.14	±.63	3.71	1.08	10	6.30	±.97	7.35	4.53	10	533	±3	541	526	10	.650	±.010	.667	.626
9.5	±1.4	11.3	6.8	4	2.6	±.5	3.7	1.9	4	8.3	±.9	6.6	3.5	4	551	±4	558	547	4	.649	±.006	.659	.637
9.18	±.45	9.97	8.33	10	1.69	±.22	2.15	1.48	10	7.55	±.79	8.72	5.36	10	549	±5	560	538	10	.677	±.007	.693	.652
9.01	±0.60	------	------	48	2.25	±0.58	------	------	48	6.64	±0.58	------	------	48	541.8	±3	------	------	48	0.6577	±0.006	------	------
8.5	±0.07	8.7	8.4	7	2.6	±0.10	2.8	2.5	7	6.0	±0.29	6.5	5.3	7	541.5	±2	547	541	7	0.653	±0.003	0.656	0.648
8.48	±.10	8.7	8.3	5	2.59	±.10	2.65	2.35	5	6.56	±.19	6.85	6.35	5	544	±2	546	541	5	.656	±.002	.661	.656
9.72	±.23	10.01	9.35	10	2.62	±.16	2.34	1.73	10	7.11	±.27	7.67	6.70	10	545	±2	549	542	10	.661	±.002	.667	.658
9.05	±0.15	------	------	22	2.33	±0.15	------	------	22	6.63	±0.26	------	------	22	544	±2	------	------	22	0.6578	±0.002	------	------
9.32	±0.34	9.75	8.80	7	1.98	±0.23	2.35	1.70	7	6.64	±0.16	6.95	6.25	7	531	±4	532	527	7	0.650	±0.002	0.653	0.646
7.47	±.19	8.03	7.10	10	2.84	±.20	3.20	2.40	10	6.69	±.13	7.07	6.40	10	528	±2	531	523	10	.656	±.001	.660	.654
8.11	±.29	8.6	7.6	10	3.15	±.27	3.6	2.8	10	6.10	±.14	6.4	5.8	10	538	±3	544	533	10	.654	±.002	.658	.651
8.19	±0.27	------	------	27	2.73	±0.27	------	------	27	6.46	±0.14	------	------	27	532.5	±3	------	------	27	0.6537	±0.002	------	------
8.97	±0.05	------	------	2	2.80	------	------	------	2	7.07	±0.005	------	------	2	539.6	±0.6	------	------	2	0.6597	±0.0003	------	------
8.79	±0.39	------	------	99	2.41	±0.39	------	------	99	6.60	±0.38	------	------	99	538.7	±2.8	------	------	99	0.6567	±0.004	------	------
8.50	±0.10	8.75	8.40	9	2.87	±0.08	3.00	2.80	9	6.12	±0.08	6.30	6.00	9	545	±1	547	544	9	0.644	±0.002	0.654	0.640
8.1	±.41	8.9	7.2	10	3.1	±.15	3.5	2.8	10	6.3	±.23	6.8	5.8	10	546	±2	555	543	10	.656	±.002	.659	.651
8.6	±.30	9.0	8.1	8	2.4	±.20	2.7	2.1	8	6.4	±.30	6.8	5.2	8	543	±4	555	539	8	.649	±.002	.652	.647
8.07	±.38	9.03	7.71	10	3.20	±.21	3.68	2.74	10	6.29	±.34	7.12	5.57	10	549	±6	560	538	10	.650	±.003	.656	.646
8.54	±.30	8.9	7.8	10	2.43	±.22	2.7	1.8	10	6.78	±.43	8.4	6.3	10	540	±5	546	522	10	.647	±.001	.650	.643
8.51	±.07	8.69	8.39	10	2.97	±.07	3.11	2.83	10	5.82	±.05	5.90	5.64	10	547	±1	549	545	10	.645	±.001	.648	.643
7.75	±.27	8.65	7.00	7	3.25	±.33	3.70	2.65	7	6.00	±.29	6.35	5.35	7	538	±2	544	536	7	.647	±.002	.647	.642
8.41	±.12	8.6	8.2	9	2.79	±.11	3.0	2.4	9	7.02	±.20	7.9	6.8	9	543	±4	549	534	9	.652	±.002	.656	.647
8.33	±0.24	------	------	73	2.88	±0.17	------	------	73	6.35	±0.24	------	------	73	544.4	±3	------	------	73	0.649	±0.002	------	------
8.6	±0.14	9.0	8.3	8	2.7	±0.14	3.0	2.5	8	5.9	±0.12	6.2	5.6	8	545	±2	550	543	8	0.647	±0.001	0.650	0.645
8.84	±1.36	11.07	6.64	5	2.78	±.37	3.30	2.28	5	5.33	±.90	7.58	4.09	5	548	±11	565	521	5	.637	±.006	.650	.624
9.06	±.06	9.23	8.98	5	2.95	±.05	2.99	2.82	5	6.46	±.27	6.98	5.13	5	549	±2	551	546	5	.641	±.001	.643	.637
8.50	±.30	8.9	7.9	5	3.03	±.13	3.2	2.9	5	6.10	±.30	6.5	5.5	5	550	±2	558	547	5	.647	±.002	.656	.644
8.67	±0.40	------	------	23	2.84	±0.17	------	------	23	5.72	±0.13	------	------	23	547.6	±4	------	------	23	0.6435	±0.002	------	------
8.41	±0.28	------	------	96	2.87	±0.17	------	------	96	6.20	±0.21	------	------	96	545.0	±3.3	------	------	96	0.6480	±0.002	------	------
8.60	±.34	------	------	195	2.64	±.28	------	------	195	6.40	±0.30	------	------	195	543.1	±3.0	------	------	195	.6519	±.003	------	------
14.80	±0.04	14.89	14.39	------	------	------	------	------	10	6.25	±0.05	6.36	6.10	10	547	±1.0	548	545	10	0.6485	±0.001	0.650	0.646
16.62	±.51	17.06	15.84	------	------	------	------	------	3	5.70	±.27	6.10	5.33	3	548	±3	552	545	3	.650	±.001	.651	.649
14.39	±.04	14.50	14.34	------	------	------	------	------	10	5.74	±.06	5.82	5.61	10	546	±.6	547	545	10	.648	±.0003	.643	.642
14.70	±.07	14.80	14.51	------	------	------	------	------	5	5.74	±.12	5.97	5.44	5	546	±.4	546	545	5	.645	±.001	.647	.644
14.72	±0.10	------	------	------	------	------	------	------	28	5.92	±0.09	------	------	28	546.6	±0.9	------	------	28	0.648	±0.001	------	------
------	±.31	------	------	195	2.64	------	------	------	223	6.34	±.27	------	------	223	543.5	±2.9	------	------	223	.6514	±.0027	------	------
------	------	11.32	6.64	------	------	------	3.71	1.08	------	------	------	8.72	3.5	------	------	------	565	520	------	------	------	0.693	0.624
------	------	11.07	6.8	------	------	------	3.68	1.70	------	------	------	8.4	4.09	------	------	------	560	521	------	------	------	.670	.626

easured value. However, the third analysis is in reasonable agreeent with the volumetric chemical analyses by the conventional ethods, with differences varying from 0.1 to about 1 percent among e various components. These differences are noted in columns 6 d 7. The heating value calculated from the third analysis by the ectrometer was 3 Btu higher than the measured value, whereas at computed from the chemical methods was 3 or 4 Btu lower. e computed specific gravity by the spectrometer was 0.6565, as mpared with 0.6476 and 0.648 by the chemical methods, and 6475±0.00007 by direct measurement. This index of composition vors the chemical methods, which is strange in view of the fact at it is known they are not capable of yielding the complete comsition of such a mixture, whereas the mass spectrometer presumably .

It will be noted that propylene and propane were identified in the ird spectrometer series, whereas these constituents were not found the first two. All of these samples were taken from the same cylinr where the standard mixture is stored under pressure and could be rtified to be of uniform composition, except for minor changes hich might occur by prolonged contact with phosphoric acids formed the P_2O_5 used for drying. If such reactions had occurred, the first mple, which was not passed over P_2O_5, should have contained proylene in the greatest amount; but no propylene was identified in this mple, nor in the succeeding dried sample, whereas the third sample, so dried, contained 0.04 percent. It would be difficult to lose 0.21 rcent of propane in a quick passage of the sample over P_2O_5, yet this mount appears in one dried sample and none was found in the other ried sample, or in the undried sample. There is no reason to suppose at the three successive portions withdrawn from the cylinder and delivered, either through P_2O_5 or not, were not all of the same composiion to well within the significance represented by the resolution of the ectrometer itself.

If the third analysis employing improved technics is accepted as rrect, it will be interesting to compute what errors were made in mputing the heating value from the analytical data derived fro e chemical methods. If the sample actually contained 0.04 percen propylene, all of the computed heating values from absorptio nalyses would have been 0.3 Btu too low. Also, if the sample conained 0.21 percent of propane, the combustion analyses would have ielded a computed heating value 0.3 Btu too low. Together, these rrors would total 0.6 Btu—not enough to explain the general low verage noted. If the sample contained 3.2 percent of ethane, the eating value computed from combustion analyses (method III) ould have been 2.7 Btu too low. For the NBS analyses, the heating alue computed was 546 Btu. Corrected for ethane, propane, and ropylene found by the mass spectrometer (third series of analyses), his value would be changed to 549.3, to agree with the measured alue (Junker's).

TABLE 3.—*Analysis of Standard Gas Sample ASTM D–3–VII–1 (carbureted water-gas type)*

[Complete report of the 24 cooperating laboratories. The starred values are omitted from the averages.]

Laboratory No.	Apparatus	Method	Analysis No.	CO_2	O_2	C_2H_4	CO	H_2	CH_4	C_2H_6	N_2	Total	Btu/ft³	Specific gravity	As reported by laboratories [1]	
															Btu	sp gr
1	2a	2b	3	4	5	6	7	8	9	10	11	12	13	14	15	16
				%	%	%	%	%	%	%	%	%				
			1	4.40 Min	0.60 Min	12.85	29.20	35.35 Max	8.60	2.90	6.10		546	0.643		
			2	4.45	.65	13.00 Max	29.10	35.10 Min	8.40 Min	3.00 Max	6.30 Max		547 Max	.654 Max		
			3	4.40	.85 Max	12.70 Min	29.10	35.25	8.65	2.85	6.20		542 Min	.644		
			4	4.40	.75	12.85	29.20	35.20	8.65	2.90	6.05		547	.644		
			5	4.45	.80	12.85	29.20	35.30	8.65	2.80	6.05		544	.644		
		II–1–1	6	4.50 Max	.80	12.80	29.20	35.30	8.65	3.00	6.00 Min		545	.645		
			7	4.40	.85	12.80	29.00 Min	35.30	8.40	2.80	6.15		544	.642		
			8	4.40	.80	12.80	29.10	35.25	8.70	2.90	6.20		545	.644		
			9	4.40	.65	12.80	29.30 Max	35.35	8.55	2.90	6.05		544	.640 Min		
1	V_1R_1Hg Burrell (0.17).		Avg.	4.42±0.03	0.75±0.08	12.83±0.05	29.16±0.07	35.27±0.06	8.59±0.10	2.87±0.08	6.12±0.08		545±1.2	0.644±0.002		
			1	4.35 Min	0.65	12.90 Max	30.30 Max	33.50 Min	8.90	2.35 Min	7.05		538	0.652 Min		
			2	4.45	.75 Max	12.70 Min	30.30	33.50	8.60 Min	2.60	7.10 Max		537 Min	.659 Max		
			3	4.45	.70	12.85	30.10 Min	33.70	8.70	2.50	7.00		538	.657		
			4	4.50 Max	.65	12.90	30.10	33.75 Max	8.80	2.70	6.60		543 Max	.656		
		I–1–1	5	4.45	.60 Min	12.85	30.10	33.75	8.60	2.80 Max	6.85		542	.657		
			6	4.50	.70	12.75	30.10	33.65	8.70	2.70	6.90		539	.658		
			7	4.50	.70	12.90	30.30	33.55	9.10 Max	2.50	6.45 Min		543	.656		
			Avg.	4.46±0.03	0.68±0.04	12.84±0.06	30.19±0.10	33.63±0.10	8.77±0.14	2.59±0.12	6.85±0.19		540±3	0.656±0.002		
			1	4.35	0.90	12.55	30.05	34.20	9.10	2.10	6.75		531.1	0.651	540.5	
			2	4.35	1.00	12.65	30.10	33.75 Min	9.70	1.70 Min	6.75		530.3	.653 Max	539.7	
			3	4.35	1.10 Max	12.60	30.05	33.85	9.75 Max	1.70	6.60		530.2	.651	539.6	
			4	4.35	1.10	12.50	29.80 Min	34.20	9.70	1.75	6.60		529.3	.649	538.7	
		I–1–2	5	4.40 Max	1.10	12.55	29.95	34.20	9.10	2.15	6.55		531.7	.652	541.0	
			6	4.20 Min	.90	12.10 Min	30.25 Max	34.45	8.80 Min	2.35 Max	6.95 Max		526.7 Min	.650	545.5	
			7	4.25	.80 Min	12.70 Max	30.10	34.70 Max	9.10	2.10	6.25 Min		535.1 Max	.646 Min	544.7	
2	$V_1R_1H_3O$ Elliott-Burrell (0.04)		Avg.	4.32±0.06	0.99±0.10	12.52±0.13	30.04±0.10	34.19±0.23	9.32±0.34	1.98±0.23	6.64±0.16		530.7±0.4	0.650±0.002	541.4	
			8	4.30 Min	0.80 Min	13.10 Max	30.00	34.15	9.40	1.75	6.50		536.4	0.650 Min	545.8	
			9	4.35	1.05 Max	13.10	29.65 Min	33.60 Min	9.70 Max	1.55 Min	7.00 Max		532.9 Min	.654 Max	542.3	
		I–1–1	10	4.40 Max	.90	13.00 Min	30.15 Max	34.20 Max	8.55 Min	2.40 Max	6.40 Min		538.3 Max	.653	547.8	
			Avg.	4.35±0.03	0.92±0.08	13.08±0.04	29.93±0.19	33.98±0.26	9.22±0.44	1.90±0.33	6.63±0.24		536.1±2	0.652±0.002	545.2	
			11	4.30	0.95	13.25	29.70	33.90	9.30	1.40	6.70		535.2	0.650	544.3	

			8	4.30 Min	0.80 Min	13.10 Max	30.00	34.15	9.40	1.75	6.50		536.4	0.630 Min	545.8	
			9	4.35	1.05 Max	13.10	29.65 Min	33.60 Min	9.70 Max	1.55 Min	7.00 Max		532.9 Min	.654 Max	542.3	
			10	4.40 Max	.90	13.00 Min	30.15 Max	34.20 Max	8.55 Min	2.40 Max	6.40 Min		538.3 Max	.653	547.8	
		I-1-1	Avg.	4.35±0.03	0.92±0.08	13.08±0.04	29.98±0.19	33.98±0.26	9.22±0.44	1.90±0.33	6.63±0.24		536.1±2	0.652±0.002	545.2	
			11	4.30	0.85	12.90	29.70	33.85	9.20	1.80	6.60		535.9	0.657	545.2	
			1	4.4 Min	0.8	12.9	30.1	34.3	7.8	3.3	6.4		545.9	0.657		
			2	4.5 Max	.8	12.8 Min	30.0	34.6 Max	8.0	3.1	6.2		542.7 Min	.654		
			3	4.5	.8	13.2	30.2 Max	34.5	7.9	3.1	5.8 Min		548.5	.655		
			4	4.5	.6 Min	13.4 Max	30.1	34.6	7.2 Min	3.5 Max	6.1		551.7	.657		
			5	4.4	.9 Max	12.8	29.6 Min	34.4	8.9 Max	2.8 Min	6.2		554.7 Max	.651 Min		
			6	4.5	.8	13.0	29.6	34.4	8.9	2.8	6.0		547.9	.652		
			7	4.5	.8	13.0	30.0	34.4	8.0	3.1	6.2		545.3	.655		
			8	4.5	.8	13.0	29.7	34.0 Min	8.0	3.2	6.8 Max		544.9	.659 Max		
			9	4.5	.8	13.0	29.7	34.0	8.3	3.0	6.7		544.4	.658		
			10	4.5	.8	13.0	30.0	34.3	7.9	3.2	6.3		545.8	.657		
3	$V_{1+2}R_1Hg$ U. S. Steel-Burrell-Modified (0.12)	II-1-1	Avg.	4.5±0.02	0.8±0.03	13.0±0.11	29.9±0.20	34.4±0.15	8.1±0.41	3.1±0.15	6.3±0.23		546.0±2	0.656±0.002	555.4	
			1	4.5 Max	0.8	12.9 Min	29.6 Max	35.1 Max	8.4	2.9	5.8		545.2	0.6475	555	
			2	4.5	.7 Min	13.0	29.6	34.9 Min	9.0 Max	2.5 Min	5.8		545.2	.6453 Min	555	
			3	4.5	.9 Max	13.0	29.6	34.9	8.3 Min	3.0 Max	5.8		547.0	.6499 Max	557	
			4	4.4	.9	13.1 Max	29.5	34.9	8.7	2.9	5.6 Min		550.4 Max	.6475	560	
			5	4.3 Min	.9	13.1	29.4	35.0	8.6	2.7	6.0		545.9	.6462	556	
		II-2-1	6	4.5	.9	13.1	29.1 Min	35.1	8.5	2.6	6.2 Max		542.5 Min.	.6469	552	
			7	4.5	.8	13.1	29.6	34.9	8.6	2.6	5.9		544.5	.6483	555	
			8	4.4	.8	13.0	29.6	35.0	8.6	2.7	5.9		545.0	.6468	555	
			Avg.	4.5±0.05	0.8±0.06	13.0±0.06	29.5±0.12	35.0±0.08	8.6±0.14	2.7±0.14	5.9±0.12		544.6±2	0.6473±0.001	555.6	
4	V_1R_1Hg Burrell-U. S Steel (0.70)		1	4.5	0.8	13.0 Min	30.5 Max	34.1 Min	8.4 Min	2.7	6.0		542.9	0.6562 Max	552	
			2	4.5	.9	13.1 Max	30.2	34.1	8.5	2.6	6.1		542.8	.6559	552	
			3	4.5	.7 Min	13.0	30.2	34.1	8.7 Max	2.5 Min	6.3		541.5	.6546	551	
			4	4.5	.8	13.0	30.2	34.1	8.3	2.7	6.2		543.0	.6558	553	
		I-2-1	5	4.3 Min	1.0 Max	13.1	29.9	34.1	8.6	2.5	6.5 Max		541.1 Min	.6545	551	
			6	4.6 Max	0.9	13.1	29.8 Min	35.0 Max	8.6	2.7	5.3 Min		547.2 Max	.6479 Min	557	
			7	4.5	.9	13.0	30.0	34.5	8.5	2.8 Max	5.8		545.4	.6524	555	
			Avg.	4.5±0.04	0.9±0.09	13.0±0.04	30.1±0.19	34.3±0.27	8.5±0.07	2.6±0.10	6.0±0.29		541.5±2	0.6530±0.003	553	
			1	4.39	0.65	13.09	29.35	31.71	14.48		6.33	100.00	546	0.649		
			2	4.39	.66	13.08	29.45	31.61 Min	14.51		6.30	100.00	546	.650 Max		
			3	4.38	.69 Max	13.04	29.42	31.72	14.39 Min		6.36 Max	100.00	545 Min	.650		
			4	4.40	.64	13.11	29.34	31.83	14.46		6.22	100.00	547	.648		
			5	4.41	.61	13.00 Min	29.44	31.87	14.48		6.20	100.01 Max	546	.648		
			6	4.37	.59	13.00	29.39 Max	31.76	14.59 Max		6.10 Min	100.00	547	.648		
			7	4.37	.59	13.14	29.42	31.70	14.51		6.26	99.99 Min	548 Max	.649		
			8	4.40	.60	13.06	29.30	31.79	14.56		6.28	99.99	547	.648		
			9	4.43 Max	.53 Min	13.18 Max	29.33	31.70	14.53		6.30	100.00	548	.649		
5	V_1R_1Hg Shepherd (0.03)	III-1-1	10	4.35 Min	.55	13.13	29.25 Min	31.99 Max	14.47		6.25	99.99	547	.646 Min		
			Avg.	4.39±0.02	0.61±0.04	13.08±0.05	29.39±0.08	31.77±0.08	14.50±0.04		6.26±0.05	100.00	546.7±1	0.6485±0.0007		

TABLE 3.—*Analysis of Standard Gas Sample ASTM D–3–VII–1 (carburetted water-gas type)*—Continued

Laboratory No.	Apparatus	Method	Analysis No.	CO_2	O_2	C_nH_m	CO	H_2	CH_4	C_2H_6	N_2	Total	Btu/ft³	Specific gravity	As reported by laboratories[1]	
															Btu	Sp gr
1	2a	2b	3	4	5	6	7	8	9	10	11	12	13	14	15	16
				%	%	%	%	%	%	%	%	%				
6	V_1R_1Hg U. S. Steel (0.02)	I-2-1	1	4.50 Min	0.90	13.45 Max	29.65 Min	33.60	8.50	2.65 Max	6.75		546 Max	0.660		
			2	4.50	1.00 Max	13.40	29.75	33.45 Min	8.70 Max	2.35 Min	6.85 Max		541 Min	.661 Max		
			3	4.60 Max	0.85	13.10 Min	30.05 Max	33.95	8.30 Min	2.65	6.50		541	.658		
			4	4.55	.80 Min	13.25	29.95	33.95	8.50	2.65	6.35 Min		545	.657		
			5	4.55	.85	13.25	29.95	34.00 Max	8.40	2.65	6.35		545	.656 Min		
			Avg.	4.54±0.03	0.88±0.06	13.29±0.11	29.87±0.14	33.79±0.21	8.48±0.10	2.59±0.10	6.56±0.19		543.6±2	0.658±0.002		
7	V_2R_2Hg Modified Hempel (0.05)	I-1-1	1	3.96 Min	0.99	12.72	30.17 Max	32.99 Min	10.00 Min	0.98 Min	8.19 Max		519.6 Min	0.655 Max		
			2	4.2	.84 Min	12.7 Min	29.84	33.55	10.59 Max	1.06 Max	7.22 Min		527.2	.649		
			3	4.3 Max	.94	12.9	29.65	34.03 Max	11.32*	0.54*	6.32*		529.5 Max	.642 Min		
			4	4.3	1.15 Max	12.98 Max	29.13 Min	33.43	10.44	0.99	7.58		526.8	.652		
			Avg.	4.19±0.12	0.98±0.09	12.83±0.10	29.70±0.41	33.50±0.29	10.59±0.37	0.89±0.18	7.33±0.56		526±3	0.650±0.004	534.8	
8	V^1R^1Hg Bureau of Mines	I-1-1	1	4.4	0.7	13.2	30.1	34.7	8.1	3.0	5.8		549.0	0.660		
			2	4.4	.8 Max	13.2	29.9 Min	34.4	9.0 Max	2.6 Min	5.7		549.4	.651 Min		
			3	4.5 Max	.6 Min	13.1	30.1	34.5	8.4	2.9	5.9		548.0	.661		
			4	4.5	.6	13.0 Min	30.1	34.4	7.6	3.4	6.4		546.9 Min	.665		
			5	4.4	.7	13.1	30.0	34.4	8.4	3.0	6.0		549.2	.653		
			6	4.4	.7	13.3	30.2 Max	34.2 Min	7.4	3.4	6.4		549.4	.660		
			7	4.4	.6	13.2	30.1	34.2	6.9 Min	3.5 Max	7.1 Max		544.2	.670 Max		
			8	4.5	.6	13.3	30.1	34.6	7.0	3.5	6.4		548.1	.666		
			9	4.3 Min	.7	13.3	30.2	34.8 Max	7.6	3.5	5.6 Min		555.2 Max	.653		
			10	4.5	.6	13.4 Max	30.0	34.6	7.2	3.5	6.2		551.4	.657		
			Avg.	4.43±0.06	0.66±0.06	13.21±0.09	30.08±0.07	34.5±0.2	7.8±0.6	3.2±0.3	6.2±0.35		549.0±2	0.656±0.006	558.6	
9	V^1R^1Hg U. S. Steel (0.23)	II-1-1	1	3.6*	0.6*	13.6*	29.9*	34.8*	8.2*	2.7*	6.6*		551*	0.646*		
			2	4.3*	.7*	13.7*	28.9*	33.0*	11.1*	1.4*	6.9*		550*	.653*		
			3	4.3 Min	.8 Max	13.2	29.3 Min	34.8	8.6	2.4	6.6		541	.651		
			4	4.3	.8	13.2	29.4	34.7	8.1 Min	2.7 Max	6.8 Max		542	.651		
			5	4.4	.6 Min	13.2	29.4	34.8	8.9	2.1 Min	6.6		539 Min	.647		
			6	4.5 Max	.8	13.4	29.5 Max	34.9	9.0 Max	2.7	5.2 Min		555 Max	.647		
			7	4.5	.6	13.4	29.5	34.6 Min	8.8	2.1	6.5		541	.649		
			8	4.5	.6	13.5 Max	29.3	34.7	8.1	2.6	6.7		544	.652 Max		
			9	4.4	.6	13.3	29.4	34.6	8.8	2.4	6.5		545	.649		
			10	4.5	0.6	13.1 Min	29.5	35.1 Max	8.6	2.3	6.3		540	.646 Min		
			Avg.	4.42±0.07	0.68±0.06	13.28±0.11	29.41±0.06	34.8±0.1	8.6±0.3	2.4±0.2	6.4±0.3		545±4	0.649±0.002	552.72	

			10	4.5	0.6	13.1 Min	29.5	35.1 Max	8.6	2.3	6.3		545	.646 Min		
			Avg.	4.43±0.07	0.68±0.08	13.28±0.11	29.41±0.00	34.8±0.1	8.6±0.3	2.4±0.2	6.4±0.3		545±4	0.649±0.002	552.72	
10	V_1R_1Hg Burrell (0.20)	II-1-1	1	4.45	0.51	12.79 Min	30.35	34.83	9.03 Max	3.26	6.09		556.3	.6454	556.1	
			2	4.40	.50 Min	13.00	29.09	34.63	8.40	3.40	7.12 Max		559.7 Max	.6464 Min	569.5	
			3	3.61*	.60	13.53 Max	28.65 Min	34.69	7.58	2.87	6.34		537.8 Min	.6526	547.2	
			4	4.31 Min	.59	12.82	30.74 Max	34.75	7.71	3.04	6.45		545.6	.6534	555.3	
			5	4.42	.59	13.26	29.87	34.58	7.75	3.68 Max	6.19		553.1	.6481	557.9	
			6	4.33	.60	12.99	29.20	35.26	8.03	2.74 Min	6.76		538.6	.6523	545.7	
			7	4.31	.69 Max	12.93	29.97	34.57	8.67	3.18	5.83		555.4	.6561 Max	565.2	
			8	4.33	.69	13.18	30.19	33.93 Min	7.48 Min	3.27	6.52		541.8	.6483	548.5	
			9	4.52 Max	.69	12.87	29.18	35.47 Max	8.02	3.26	6.15		550.1	.6472	556.9	
			10	4.41	.69	13.12	29.09	35.26								
			Avg.	4.45±0.08	0.62±0.06	13.05±0.18	29.63±0.39	34.82±0.35	8.07±0.38	3.20±0.21	6.29±0.34		548.8±6	0.6502±0.003	556.1	
11	V_1R_1Hg Shepherd (0.01)	III-1-1	1	4.37 Max	0.54	11.59 Min	30.48	30.42 Min	16.95		5.66		546.5	0.6507 Max		
			2	4.20 Min	.59 Max	11.83	30.53 Max	30.53	17.06 Max		5.33 Min		551.9 Max	.6488 Min		
			3	4.33	.45 Min	12.15 Max	30.21 Min	30.91 Max	15.84 Min		6.10 Max		545.0 Min	.6503		
			Avg.	4.30±0.07	0.53±0.05	11.86±0.20	30.41±0.13	30.62±0.19	16.62±0.51		5.70±0.27		547.8±3	0.6499±0.001		
12	V_1R_1Hg Burrell (0.05)	I-1-1	1	4.33 Min	0.82	13.08	30.50	36.25 Max	7.48 Min	3.37	4.53 Min		541 Max	0.635	550	
			2	4.48	.81	13.13	30.10	35.10	7.56	3.71 Max	5.80		533	.649	542	
			3	4.48	.82 Max	13.27 Max	31.55 Max	33.20	9.08	2.04	6.23		534	.658	543	
			4	4.48	.82	13.16	31.00	33.07 Min	8.88	2.45	7.14		535	.665	544	
			5	4.44	.81	13.13	30.70	33.80	9.23	2.15	5.65		534	.645	543	
			6	4.44	.72 Min	13.13	31.00	33.55	9.88	1.78	5.54		534	.645	543	
			7	4.43	.80	13.07	30.04	33.60	9.86	1.81	7.35		530	.654	539	
			8	4.52 Max	.80	12.97 Min	30.65	33.58	9.95	1.71	6.91		530	.655	539	
			9	4.44	.81	13.02	30.08	33.72	10.75 Max	1.08 Min	8.68 Max		526 Min	.667 Max	535	
			10	4.33	.81	13.00	29.71 Min	34.42	10.62	1.28	5.13		530	.626 Min	539	
			Avg.	4.44±0.04	0.80±0.02	13.10±0.07	30.53±0.45	34.03±0.75	9.33±0.88	2.14±0.63	6.30±0.97		533±3	0.650±0.010	542	
13	V_1R_1Hg Burrell (built-up) (0.0)	II-1-1	1	4.3	0.7	13.2	28.9	34.9	7.8 Min	1.8 Min	8.4 Max		535	0.647	550.966	(Density 0.8397858
			2	4.3	.7	12.7 Min	29.3 Max	35.1	8.1	2.7 Max	7.1		522 Min	.650 Max	543.983	.8366846
			3	4.4 Max	.9 Max	13.3 Max	28.9	34.9	8.9 Max	2.3	6.4		543	.646	552.696	.8354037
			4	4.3	.8	13.1	28.8	35.2 Max	8.8	2.4	6.6		541	.643 Min	550.895	.8316517
			5	4.4	.8	13.2	29.2	34.8	8.6	2.7	6.3 Min		546 Max	.648	555.836	.8283964
			6	4.4	.8	13.1	29.0	34.9	8.6	2.6	6.6		543	.647	552.113	.8371401
			7	4.4	.9	13.3	28.7 Min	35.2	8.2	2.7	6.6		544	.647	553.063	.8361014
			8	4.2 Min	.6 Min	13.2	29.3	34.7 Min	8.9	2.1	7.0		539	.646	548.138	.8355508
			9	4.3	.8	13.2	29.0	35.0	8.8	2.5	6.4		545	.645	554.293	.8340749
			10	4.4	.8	13.2	29.1	34.9	8.7	2.5	6.4		546	.647	553.274	.8364959
			Avg.	4.34±0.06	0.78±0.07	13.14±0.11	29.02±0.16	34.96±0.13	8.54±0.30	2.43±0.22	6.78±0.43		540±5	0.647±0.001	550	

TABLE 3.—*Analysis of Standard Gas Sample ASTM D–3–VII–1 (carburetted water-gas type)*—Continued

Laboratory No.	Apparatus	Method	Analysis No.	CO_2	O_2	C_2H_4	CO	H_2	CH_4	C_3H_8	N_2	Total	Btu/ft³	Specific gravity	As reported by laboratories[1]	
															Btu	Sp gr
1	2a	2b	3	4	5	6	7	8	9	10	11	12	13	14	15	16
				%	%	%	%	%	%	%	%	%				
14	V_1R_1Hg Shepherd-Burrell	II–1–1	1	4.40 Min	0.60 Min	12.81	29.58	35.44 Max	8.45	3.03	5.82	100.16	548	0.644		
			2	4.45	.60	12.91 Max	29.33	35.29	8.45	3.03	5.90 Max	99.96	548	.644		
			3	4.50	.70	12.91	29.53	35.09 Min	8.51	3.00	5.84	100.08	548	.647		
			4	4.56	.80 Max	12.79	29.48	35.20	8.48	2.98	5.88	100.17	546	.648 Max		
			5	4.52	.70	12.76 Min	29.25 Min	35.22	8.45	3.01	5.87	99.78 Min	545 Min	.644		
			6	4.43	.70	12.78	29.51	35.44	8.55	2.91	5.80	100.12	546	.645		
			7	4.50	.65	12.85	29.65	35.25	8.39 Min	3.11 Max	5.77	100.17	549 Max	.643 Min		
			8	4.50	.70	12.81	29.43	35.24	8.64	2.83 Min	5.76	99.91	545	.644		
			9	4.55 Max	.60	12.80	29.90 Max	35.10	8.66	2.87	5.71	100.19 Max	547	.646		
			10	4.40	.60	12.86	29.78	35.34	8.69 Max	2.84	5.64 Min	100.15	548	.643		
			Avg.	4.49±0.04	0.67±0.05	12.83±0.04	29.52±0.12	35.25±0.08	8.51±0.07	2.97±0.07	5.82±0.05	100.07	547.0±1.1	0.6448±0.0012		
15	V_1R_1Hg U. S. Steel-Shepherd (0.0)	I–1–1	1	4.6 Max	0.6 Min	13.0	30.1	34.5								
			2	4.5	.7	13.0	30.1	34.0								
			3	4.5	.8	12.8 Min	29.9 Min	34.6	9.4	2.6	5.4		547.6	0.643		
			4	4.4 Min	.7	13.1 Max	30.2	34.5	6.8 Min	3.7 Max	6.6 Max		546.5 Min	.659 Max		
			5	4.4	.9 Max	12.9	30.3 Max	34.8 Max	11.3 Max	1.9 Min	3.5 Min		557.8 Max	.637 Min		
			6	4.5	.6	13.1	30.0	33.7 Min	10.4	2.2	5.6		552.7	.652		
			Avg.	4.48±0.06	0.71±0.08	12.98±0.09	30.10±0.10	34.35±0.30	9.5±1.4	2.6±0.5	5.3±0.9		551.3±4	0.649±0.006		
		II–1–1	7	4.6	0.8	13.0	30.6	36.5	9.2	3.0	2.3					
16	V_1R_1Hg Burrell-Oberfell (0.05)	II–1–1	1	4.55 Max	0.70 Max	12.40	29.65	35.60								
			2	4.50	.70	12.20	30.40	35.05								
			3	4.50	.70	12.05 Min	30.50 Max	34.90 Min								
			4	4.50	.70	12.05	29.95	35.90 Max	7.00 Min	3.70 Max	6.20		535.5 Min	0.6465		
			5	4.50	.60 Min	12.15	30.35	35.20	7.40	3.45	6.35 Max		535.6	.6507 Max		
			6	4.50	.60	12.25	30.25	35.25	7.75	3.45	5.95		540.6	.6489		
			7	4.50	.65	12.30	30.40	35.65	7.60	3.55	5.35 Min		543.4	.6460		
			8	4.50	.60	12.70 Max	30.05	35.75	8.10	2.70	5.60		544.0 Max	.6423 Min		
			9	4.40 Min	.60	12.70	29.70	35.35	7.70	3.35	6.20		544.0	.6477		
			10	4.50	.60	12.45	29.50 Min	35.45	8.05 Max	2.65 Min	6.20		536.9	.6428		
			Avg	4.50±0.01	0.65±0.05	12.30±0.19	30.05±0.30	35.40±0.27	7.75±0.27	3.25±0.33	6.00±0.29		537.8±2	0.6465±0.002	538.7	
			1	4.45	0.70 Min	13.85 Max	29.25	33.05	9.90	1.85	6.95		549.1 Max	0.658 Min	851.1	
			2	4.65 Max	.80	13.65	29.10 Min	32.80	9.94	1.73 Min	7.33		542.9	.662	855.4	
			3	4.55	.80	13.55	29.35	33.05	9.61	1.97	7.12		544.0	.660	853.6	
			4	4.60	.80	13.35 Min	29.35	33.10	9.91	1.97	6.72		543.9	.659	851.9	

17	V_1R_1Hg Burrell-Build-up (0.03)	I-2-1	1	4.45	0.70 Min	13.85 Max	29.25	33.05	9.90	1.85	6.95	....	549.1 Max	0.658 Min	851.1	....
			2	4.65 Max	.80	13.65	29.10 Min	32.80	9.94	1.73 Min	7.33	....	542.9	.662	855.4	....
			3	4.55	.80	13.55	29.35	33.05	9.61	1.97	7.12	....	544.0	.660	853.6	....
			4	4.60	.80	13.35 Min	29.35	33.10	9.91	1.97	6.72	....	543.9	.659	851.9	....
			5	4.60	.80	13.50	29.50	33.30 Max	9.40	2.20	6.70 Min	....	546.3	.659	852.4	....
			6	4.60	.80	13.48	29.48	33.10	9.35 Min	2.34 Max	6.92	....	547.3	.661	854.7	....
			7	4.53	.75	13.60	29.25	33.00	10.01 Max	1.77	7.02	....	544.6	.659	852.2	....
			8	4.60	.85	13.40	29.55 Max	32.30	9.66	2.07	7.67 Max	....	542.0 Min	.667 Max	862.0	....
			9	4.50	.90 Max	13.65	29.35	32.95	9.44	2.23	6.98	....	548.0	.662	856.0	....
			10	4.43 Min	.82	13.40	29.49	32.28 Min	9.96	2.02	7.60	....	543.0	.665	859.9	....
			Avg.	4.54±0.06	0.80±0.03	13.56±0.10	29.36±0.11	32.91±0.26	9.72±0.23	2.02±0.16	7.11±0.27	....	545.2±2	0.661±0.002	854.9	....
18	V_1R_1Hg S. Cal. Co.-Burton (0.0)	II-2-1 Analyst 1	1	4.61 Max	1.15 Max	12.67 Min	28.59	35.29 Min	9.10	3.30 Max	5.29	....	553	0.650 Max	553.0	....
			2	4.51	0.62	13.03	28.31 Min	37.03	6.64 Min	2.28 Min	7.58 Max	....	520.9 Min	.638	520.9	....
			3	4.38 Min	.71	12.95	29.15 Max	36.70	7.59	3.19	5.33	....	546.5	.637	546.5	....
			4	4.44	.61	13.13	28.89	37.78 Max	8.28	2.78	4.09 Min	....	551.9	.624 Min	551.9	....
			5	4.47	.53 Min	13.21 Max	28.65	35.36	11.07 Max.	2.34	4.37	....	564.7 Max	.634	564.7	....
			Avg.	4.48±0.06	0.72±0.15	13.00±0.15	28.72±0.24	36.43±0.62	8.54±1.26	2.78±0.37	5.33±0.90	....	548±11	0.637±0.006	....	....
		II-2-1 Analyst 2	1′	4.33 Min	0.52 Max	12.37	29.48	35.26 Min	9.08	2.98	5.98 Max	....	545.1	0.643 Max	....	....
			2′	4.36	.52	12.34 Min	29.67 Max	35.37	9.14	2.99 Max	5.61	....	546.4 Min	.642	....	....
			3′	4.46 Max	.32 Min	12.65	29.44	36.03 Max	8.98 Min	2.99	5.13 Min	....	551.2 Max	.637 Min	....	....
			4′	4.44	.52	12.81 Max	29.34 Min	35.54	9.23 Max	2.82 Min	5.30	....	551.2	.641	....	....
			5′	4.36	.52	12.67	29.60	35.62	8.99	2.96	5.28	....	550.3	.641	....	....
			Avg.	4.39±0.05	0.48±0.08	12.57±0.21	29.51±0.10	35.56±0.21	9.08±0.08	2.95±0.05	5.46±0.27	....	549±2	0.641±0.001	....	....
		II-2-1 Analyst 3	1″	4.4 Min	0.6	13.1	28.8 Min	35.2	8.7	2.9 Min	6.3	....	549	0.646	....	....
			2″	4.5 Max	.5 Min	13.3 Max	29.2	35.6 Max	8.5	2.9	5.5 Min	....	553	.644 Min	....	....
			3″	4.4	.7 Max	13.2	30.9 Max	33.3 Min	2.1*	7.0*	8.4 Max	....	558 Max	.696 Max	....	....
			4″	4.5	.6	13.0 Min	28.8	35.0	8.9 Max	3.1	6.1	....	552	.648	....	....
			5″	4.4	.6	13.1	29.1	35.2	7.9 Min	3.2 Max	6.5	....	547.4 Min	.650	....	....
			Avg.	4.45±0.05	0.58±0.04	13.13±0.09	28.98±0.18	35.25±0.18	8.50±0.30	3.03±0.13	6.10±0.30	....	550±2	0.647±0.002	....	....

TABLE 3.—*Analysis of Standard Gas Sample ASTM D–3–VII–1 (carburetted water-gas type)*—Continued

Laboratory No.	Apparatus	Method	Analysis No.	CO_2	O_2	C_2H_4	CO	H_2	CH_4	C_2H_6	N_2	Total	Btu/ft³	Specific gravity	As reported by laboratories [1]	
															Btu	Sp gr
1	2a	2b	3	4	5	6	7	8	9	10	11	12	13	14	15	16
				%	%	%	%	%	%	%	%	%				
19	Gockel (0.1)	I-1-2	1	4.45	0.80	12.26	31.07	34.32	8.03 Max	2.40 Min	6.67		524.7	0.6552		
			2	4.50 Max	.80	12.40	30.80	34.40	7.51	2.92	6.67		530.4	.6573		
			3	4.48	.89	12.25	30.97	34.51	7.60	2.54	6.76		523.0 Min	.6557		
			4	4.50	.70 Min	12.30	31.10 Max	34.50	7.42	2.89	6.59		528.5	.6567		
			5	4.40 Min	.70	12.50 Max	30.90	34.80 Max	7.34	2.85	6.51		530.6	.6539 Min		
			6	4.40	.90 Max	12.32	30.75	34.73	7.10 Min	3.04	6.76		527.9	.6558		
			7	4.49	.80	12.39	30.89	34.43	7.67	2.69	6.64		527.8	.6554		
			8	4.50	.90	12.11 Min	30.91	34.58	7.42	3.18	6.40 Min		530.2	.6564		
			9	4.44	.70	12.39	30.84	34.23 Min	7.13	3.20 Max	7.07 Max		530.8 Max	.6603 Max		
			10	4.42	.90	12.35	30.72 Min	34.64	7.44	2.75	6.78		526.3	.6551		
			Avg.	4.46±0.03	0.80±0.07	12.33±0.08	30.91±0.11	34.50±0.13	7.47±0.19	2.84±0.20	6.69±0.13		528.0±2	0.6562±.001	528.3	0.6564
By Distillation (small sample)			1	4.46	0.80	12.37	30.45	34.31	7.40	3.52	6.69		538	0.664		
20	V_4R_2Hg Bone-Wheeler.	I-2-2	1	4.30	0.61	12.64	30.38	33.32	8.87	2.80	7.08		540.8	0.6600		
			2	4.32	.88	12.41	30.10	33.36	9.06	2.80	7.07		538.3	.6593		
			Avg.	4.31±0.005	0.75±0.07	12.52±0.05	30.24±0.07	33.34±0.01	8.97±0.05	2.80	7.07±0.005		539.6±0.6	0.6597±0.0003		
21	V_1R_1Hg Bureau of Mines (0.01)	II-1-1	1	4.4 Min	0.9	13.6 Max	28.8	34.2	8.3	2.8	7.0		548.1	0.656 Max		
			2	4.4	.9	13.6	28.6	34.3	8.4	2.8	7.0		548.9 Max	.654		
			3	4.4	.6 Min	13.1	29.2	34.6	8.5	2.9	6.7 Min		546.5	.651		
			4	4.4	.7	13.0 Min	29.2	34.5	8.5	2.8	6.9		542.9	.652		
			5	4.4	.7	13.1	29.3 Max	34.4	8.5	2.8	6.95		542.1	.653		
			6	4.5 Max	.7	13.0	29.3	34.5	8.2 Min	3.0 Max	6.8		543.7	.654		
			7	4.4	1.2 Max	13.3	28.4 Min	34.0 Min	8.6 Max	2.4 Min	7.9 Max		534.3 Min	.647 Min		
			8	4.4	0.9	13.1	29.0	34.6	8.5	2.7	6.9		540.8	.652		
			9	4.4	1.0	13.1	28.9	34.7 Max	8.2	2.9	7.0		538.9	.651		
			Avg.	4.41±0.02	0.84±0.15	13.13±0.21	28.97±0.26	34.42±0.18	8.41±0.12	2.79±0.14	7.02±0.20		543±4	0.652±0.002	544	0.654

			2	4.4	.12	12.5	30.1	34.3	7.9	3.3	6.3		540	0.657		
			3	4.4	.13	12.3 Min	30.3 Max	34.1	8.6 Max	2.9	6.1		537	.655		
			4	4.4	.14	12.3	30.2	34.6	8.1	2.9	6.1		533 Min	.654		
			5	4.2 Min	.14	12.5	30.0 Min	34.5	8.5	2.9	6.0		539	.651 Min		
22	V_1R_1Hg (0.07)	I-1-2	6	4.3	.12	12.4	30.2	34.4	8.3	2.8 Min	6.4 Max		534	.654		
			7	4.4	.13	12.3	30.1	34.8 Max	7.9	3.2	6.0		537	.653		
			8	4.4	.15 Max	12.3	30.0	34.6	8.5	2.9	5.8 Min		537	.652		
			9	4.4	.13	12.3	30.0	34.8	7.6 Min	3.6 Max	6.0		540	.654		
			10	4.5 Max	.13	12.4	30.0	34.6	7.7	3.5	6.0		541	.656		
			Avg.	4.38±0.05	.129±0.09	12.38±0.08	30.11±0.09	34.48±0.21	8.11±0.29	3.15±0.27	6.10±0.14		538±3	0.654±0.002		
			1	4.80	1.77 Max	14.93	29.04	31.38	8.33 Min	2.15 Max	7.60		550	0.684		
			2	4.70 Min	1.36 Min	14.90	28.92	32.13	9.70	1.89	6.40		560 Max	.670		
			3	4.71	1.47	15.21 Max	28.54	31.21	9.66	1.21	7.99		549	.678		
			4	4.76	1.38	14.81	28.56	34.29 Max	9.36	1.48 Min	5.36 Min		555	.652 Min		
	$V?R_1Hg$ Fischer Unitized (0.3)	I-1-1	5	4.77	1.51	14.91	29.47	30.33 Min	8.36	1.93	8.72 Max		544	.693 Max		
23			6	4.91 Max	1.37	14.76	28.98	31.35	9.75	1.90	7.98		547	.682		
			7	4.78	1.44	14.81	29.61 Max	30.91	9.02	1.54	7.89		555	.684		
			8	4.78	1.43	14.81	29.14	31.34	9.97 Max	1.62	6.91		555	.677		
			9	4.71	1.41	14.26 Min	28.71	31.99	9.28	1.52	8.12		538 Min	.673		
			10	4.81	1.50	15.04	28.25 Min	30.99	9.34	1.65	8.50		549	.677		
			Avg.	4.77±0.04	1.46±0.08	14.84±0.15	28.92±0.32	31.58±0.73	9.18±0.45	1.69±0.22	7.55±0.79		549±5	0.677±0.007		
			1	4.45	0.53	12.96	29.96	31.98	14.35		5.77	100.00 Max	545.6	0.6478		
			2	4.49 Max	.56	12.90 Min	29.99	31.91	14.36		5.79	100.00	544.6 Min	.6483		
			3	4.46	.61 Max	12.93	29.95	31.91	14.37		5.76	99.99 Min	545.1	.6485 Max		
			4	4.42	.49 Min	12.97	29.91 Min	31.99	14.39		5.82 Max	99.99	546.0	.6467 Min		
			5	4.43	.53	13.00 Max	29.95	32.03	14.34 Min		5.72	100.00	546.3	.6473		
			6	4.42	.55	12.99	30.01	31.94	14.37		5.73	100.00	546.4	.6478		
			7	4.40	.60	12.96	29.91	31.84 Min	14.50 Max		5.78	99.99	546.5	.6483		
			8	4.39 Min	.55	12.98	29.92	31.95	14.40		5.80	99.99	546.2	.6472		
			9	4.45	.57	12.99	29.93	31.96	14.48		5.62	100.00	547.3 Max	.6471		
			10	4.48	.55	12.94	30.02 Max	32.03 Max	14.37		5.61 Min	100.00	545.9	.6472		
24	V_1R_1Hg Shepherd (0.02)	III-1-1	Avg.	4.44±0.03	0.55±0.03	12.96±0.02	29.96±0.03	31.95±0.04	14.39±0.04		5.74±0.06		546.0±0.6	0.6476±0.001		
					0.57 Max											
			1	4.35 Min	.47	12.83	29.61	31.98	14.71		5.97 Max		545.1 Min	0.6460		
			2	4.41	.49	12.77	29.82	31.89 Min	14.80 Max		5.76		546.4 Max	.6465 Max		
			3	4.45	.53	12.71 Min	29.72	32.06	14.72		5.77		545.8	.6452		
			4	4.51 Max	.52	12.74	29.50 Min	32.23	14.75		5.79		545.9	.6436 Min		
			5	4.47	.46 Min	12.86 Max	30.03 Max	32.29 Max	14.51 Min		5.44 Min		545.4	.6441		
			6		.54	12.78										
			Avg.	4.44±0.05	0.51±0.03	12.78±0.04	29.74±0.15	32.09±0.14	14.70±0.07		5.74±0.12		545.7±0.4	0.6450±0.001		

[1] Only those data which differ from columns 13 and 14 are given.

WASHINGTON, May 24, 1945.

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